SULFAMIC ACID #101

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10575

GRAS MONOGRAPH SERIES

SULFAMIC ACID

prepared for

THE FOOD AND DRUG ADMINISTRATION
DEPARTMENT OF HEALTH, EDUCATION
AND WELFARE

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prepared by

Tracor Jitco, Inc.

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SUMMARY

Description
Sulfamic acid is a colorless, odorless, ortho-
rhombic crystalline solid. It is non-volatile, non-
hygroscopic and stable when dry. It is quite soluble
in water but slowly hydrolyzes to ammonium bisulfate.
Chemically, sulfamic acid is comparable to the strong
mineral acids.

Ammonium sulfamate is a white, odorless, crystalline
solid, further characterized by being hygroscopic. It
is extremely soluble in water. Neutral or alkaline
aqueous solutions are stable even at temperatures as
high as 100°C. It does not decompose on evaporation.

Occurrence and Consumer Exposure
Sulfamic acid and its salts are purely synthetic
substances, consequently they do not occur naturally
in foods. However, trace amounts may enter certain
foods from paper and paperboard containers which may
contain sulfamic acid or ammonium sulfamate as pro-
cessing additives (060). Moreover, zinc sulfamate
has been used in a public water system as a corrosion
inhibitor at a level of 1-3 ppm (047, 048, 068, 045).

A new sulfamate sweetener, sodium 4-thiacyclohexyl
sulfamate, was recently discovered in Germany (067).

A wide variety of foods may become contaminated
with sulfamic acid as a result of its use as an acid
cleaner for food processing and storage equipment
(053, 025 , 060).

The use of ammonium sulfamate as a week killer
represents another possible source of food con-
tamination (016, 020).

Acute Toxicity

A Minimum Lethal Dose (MLD) of 1600 mg/kg BW for rats
per os has been reported for sulfamic acid (002). The
oral LD_{50} of ammonium sulfamate (ammate) in this
animal is 3900 mg/kg BW (040). Acute toxicity values
for other experimental animals apparently have not
been published.

For man, the probable lethal dose of sulfamic acid
orally, would be 500-5,000 mg/kg BW, giving it a
toxicity rating of 3 (moderately toxic). Ammonium
sulfamate with a probable lethal dose of 500-5,000 mg/kg,
or 5,000-15,000 mg/kg BW, is rated 2 or 3 (slightly
or moderately toxic) (031).

Short-Term
Studies

Sulfamic acid or ammonium sulfamate in the diet of
rats retarded growth at a level of 2% but not at 1%.
No deaths occurred and microscopic, as well as gross,
pathological manifestations were absent (002).

In dogs, neither compound was toxic orally in doses
of 100 mg/kg over a period of six days (020). Cattle,
on the other hand, suffered extreme scouring (diarrhea)

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when fed ensilage containing 1% sulfamic acid;
there were no symptoms, however, at the 0.5% level
(017). In man, ingestion of ammonium sulfamate
causes irritant effects and gastrointestinal
disturbances; however, there is no systemic toxicity
with moderate amounts (062, 026).

Biochemistry   In mice, nickel (II) sulfamate injected intraperi-
toneally in lethal doses (500 mg/kg BW) causes
dyspnea and straining prior to death (014). Rats
receiving sulfamic acid or ammonium sulfamate in the
diet at a level of 2% were definitely retarded in
growth; also there was evidence of a slight cathartic
effect (002). Intraperitoneally, fatal doses of ammonium
sulfamate (800 mg/kg BW) stimulated respiration prior
to prostration and death (002). Dogs, injected intra-
venously with sulfamic acid or ammonium sulfamate in
doses of 100 mg/kg, manifested a slight **drop in**
blood pressure and depth of respiration but both
promptly returned to normal; doses of 20 mg/kg BW had
no effect (002). In this animal, ingested sulfamate
apparently was not metabolized but was excreted in
the urine unchanged (020).

In cattle, sulfamic acid fed at a level of 1% in
ensilage caused severe diarrhea but was tolerated
without symptoms at a level of 0.5% in the diet (017).
An anticoagulant effect of the sulfamate ion in vitro has
been reported (070).

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Safe Levels   Sulfamic acid may be present in minute trace
amounts in foods under section 121.101 h of the
Food, Drug, and Cosmetic Act as amended, 1958, (060):
"substances migrating to food from paper and paper-
board products used in food packaging that are
generally recognized as safe for their intended
use, within the meaning of section 409 of the
Act."

The California State Health Department permits* the
use of sulfamic acid or zinc sulfamate in drinking
water at a level of one part per million (047,048).

The Threshold Limit Value for ammonium sulfamate
in an atmospheric environment is 15 mg per cubic
meter of air (026).

* Use was prohibited in August, 1973 (071).

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CHEMICAL INFORMATION

Sulfamic acid, ammonium sulfamate, and zinc sulfamate appear to be the only substances of the sulfamate family requiring consideration at this time from the food additive or food contamination standpoint (047,060). However, a new fulfamate sweetening agent recently discovered in Germany, Sodium 4-thiacyclohexyl sulfamate, could assume major importance (067).

Sulfamic Acid

I. **Nomenclature**
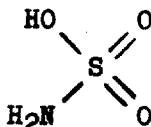
    A. Common name: Sulfamic acid

    B. Chemical name: Sulfamic acid

    C. Synonyms: Amidosulfonic acid, Amidosulfuric acid, Aminosulfonic acid, Sulphamic acid, Sulphamidic acid.

    D. Trade names: No information

    E. Chemical Abstracts Services Unique Registry Number: 5329146

II. **Empirical Formula**

$$H_3NO_3S$$
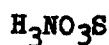
III. **Structural Formula**

IV. **Molecular Weight:**

    97.10

V. Specifications

Grades: Reagent, Crystalline, Granular (034)

A. Granular Grade, Dupont (025)

Average Analysis

Sulfamic acid, Wt. %	92.3*

U.S.S. Screen Size

On #16, Wt. %	————
Through #100, Wt. %	4.0

*Remaining 7.7% is primarily ammonium bisulfate

B. Crystal Grade, Dupont (026)

Average Analysis

Sulfamic acid, Wt. %	99.6

U.S.S. Screen Size

On #16, Wt. %	0.1-0.6
Through #100, Wt. %	————

C. Reagent Grades, G. Frederick Smith Chemical Co., Columbus, Ohio (029)

#97 Sulfamic Acid, Primary Standard

Assay	99.9%
Insolubles	0.01%
Heavy metals	0.001%
Iron	0.0005%
Chloride	0.001%
Sulfate	0.05%
Residue on ignition	0.01%

#98 Sulfamic Acid, GFS Certified

Assay	99.97-100.03%
Insolubles	0.01%
Heavy metals	0.001%
Iron	0.0005%
Chloride	0.001%
Sulfate	0.05%
Residue on ignition	0.01%

VI. Description

A. General Characteristics

Sulfamic acid is a colorless, odorless, orthorhombic crystalline solid.

B. Physical properties

The crystals melt at 205°C, with decomposition (062). The acid is soluble in water, 24.2 parts/100 parts of water at 25°C, and 125 parts/200 parts of water at 70°C (016). It is sparingly soluble in ethanol and methanol, slightly soluble in acetone, but insoluble in ether. It is freely soluble in formamide, dimethylformamide, and pyridine (062).

C. Stability in containers, etc.

Sulfamic acid is a non-volatile, non-hygroscopic solid and is stable when dry. A giant crystal wrapped in cheesecloth and stored at ordinary room conditions for four years did not change in appearance excepting for a slight loss in lustre. These properties are very unusual for an acid which is comparable in strength to hydrochloric, nitric, and sulfuric acids (020, 062). Sulfamic acid can be packaged and transported commercially without difficulty. It is, however, combustible (034).
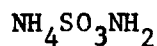
Ammonium Sulfamate

Note: This monograph was prepared primarily on the subject of sulfamic acid. However, some contributory information on the toxicity of the sulfamate radical has been determined by studies on ammonium sulfamate. Thus, although ammonium sulfamate is not the subject of the monograph pertaining to food additives, its pertinence to the problem

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prompts us to include not only the toxicity information but also the information in the following paragraphs on nomenclature, formulas, molecular weight, specifications, description, and so on.

I. <u>Nomenclature</u>

    A. Common name: Ammonium sulfamate

    B. Chemical name: Sulfamic acid, monoammonium salt

    C. Synonyms: Ammonium amidosulphate, Ammonium sulphamate

    D. Trade names: Ammate; Ammate X; Ammat

    E. Chemical Abstracts Services Unique Registry Number: 7773060

II. <u>Empirical Formula</u>

    $NH_4SO_3NH_2$

III. <u>Structural Formula</u>

$$H_2N - \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}} - O - NH_4$$
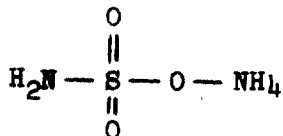
IV. <u>Molecular Weight:</u> 114.13

V. <u>Specifications</u>

    A. Crystal Grade, Dupont (026)

        Typical Analysis

Ammonium sulfamate	98.9%
Free sulfate as $(NH_4)_2SO_4$	1.1%
Iron as Fe	0.001%
Water insoluble matter	0.006%
Moisture	0.020%

B. "Ammate" brand weed killer is a brownish-gray, crystalline, hygroscopic material containing a minimum of 80% ammonium sulfamate (062).

VI. Description

A. General characteristics

Ammonium sulfamate is a white, odorless, crystalline solid which is hygroscopic. The commercial weed killer brand, Ammate, differs as described in V-B above.

B. Physical properties

Ammonium sulfamate is highly soluble in water, moderately soluble in glycerol, glycol, and formamide, but only slightly soluble in ethanol. Its melting point is 131°C. Hazard: Hot acid solutions, if enclosed, may explode (034).

C. Stability in containers, etc.

Ammonium sulfamate is hygroscopic.

VII. Analytical Methods

A. Detection

1. Steger and Stopperka (063) pointed out that bands occur in the spectrum of sulfamic acid which are analogous to those in the infrared spectra of primary amidophosphates (e.g., $NaPO_3NH_3$); the latter "exhibit bands near 2482 and 2620 cm^{-1} which are of comparable strength to the NH valence vibrations in the 2900 cm^{-1} region". These data may be of some value in detection and partial identification of sulfamic acid.

2. In a study of the importance of Rm values for the paper chromatography of ammonia derivatives of sulfuric acid, Kempe (038) gives the Rf value of sulfamic acid. The solvent system was dioxane 68.5, H_2O 31.4 and concentrated NH_4OH 0.1 ml.

3. Harlow and Morman (033) have developed an ion-exclusion partition chromatographic procedure for acids which may be applicable, under certain conditions, for the separation, partial identification, and quantitation of small amounts of sulfamic acid in foods and other materials. Salts, such as ammonium sulfamate, may be determined as the corresponding acid.

In this procedure, the acids are automatically separated on a column of sulfonated polystyrene ion exchange resin using water only as the eluent. The column effluent is titrated automatically and the titration data are recorded as a function of time. Emergence times indicate the possible identity of the acids, based on a table of emergence data constants. These were determined by Harlow and Morman for more than 50 acids including sulfamic acid.

Advantages of the method, which are pointed out by the authors, are that it is automatic, rapid, relatively specific for acids, and applicable to dilute aqueous solutions. Less than an hour is sufficient for separation with most samples, and materials other than acids generally do not interfere.

The method is not applicable for detection and identification of sulfamic acid or sulfamates in samples containing sulfonic acids, other acids (like sulfamic) which contain both an amino group and a sulfonic acid group, or mineral acids, since the emergence data of these are too similar for differentiation.

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B. Quantitation

1. Gravimetric methods. In the older gravimetric methods, sulfamate was oxidized to sulfate. Apparently the latter was then precipitated as barium sulfate (060).

2. Volumetric methods. Sulfamic acid is a strong acid and can be titrated with bases using indicators that show color change between pH 4.5 to 9.0 (062).

3. Sulfamic acid or the sulfamate ion can be determined rapidly by a direct titration method based on the following quantitative chemical reaction:

$$NH_2SO_3H + NaNO_2 \longrightarrow NaHSO_4 + H_2O + N_2$$
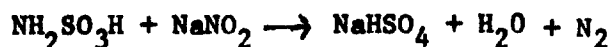
Starch-iodide is used as an external indicator. The accuracy is reported to be comparable to that of the older gravimetric methods mentioned above (009).

4. Gasometric method. A gasometric micro method, with an accuracy of $\pm$ 5%, requiring only 20 minutes, has been developed based on measurement of the nitrogen gas evolved in the reaction mentioned in the preceding paragraph (013). Santmyers and Aarons report that "the reaction is specific for the amino group and very few ions interfere" (060).

VIII. Occurrence

Sulfamic acid and its derivatives are purely synthetic substances and do not occur naturally.

A. Plants

Ammonium sulfamate is used to destroy noxious plants such as poison ivy and poison oak, agricultural pests, like ragweed and

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Canadian thistle, as well as certain other types of herbage which clutter up the environment, such as choke cherry, hoary cress, and so forth (016,062,010). It is regarded as a more effective herbicide than sodium chloride, calcium chloride, ammonium thiocyanate, or ammonium sulfate. It is as good as sodium chlorate for all herbicidal problems, and is actually more effective against some weeds. It is a fire retardant rather than a fire hazard, which is a valuable additional advantage where large areas of herbage must be destroyed. Moreover, it does not permanently sterilize the soil as do certain other herbicides, apparently being quite rapidly decomposed by certain types of soil microorganisms (016,020,041).

Another advantage of ammonium sulfamate over many other weed killers for large scale agricultural use is that it actually increases soil fertility by adding utilizable nitrogen in the form of the ammonium ion. Finally, it is regarded as non-toxic to man and lower animals (016).

No information was found in the literature concerning levels in treated plants, in adjacent edible plants and/or their fruits, and in the soil locally or generally. An estimate may be possible in the case of poison ivy on the basis of the recommended treatment:

A solution containing one pound of ammonium sulfamate per gallon of water is sprayed on the foliage while it is still green during late summer or early autumn and preferably in humid weather. (016)

The plant is killed as the salt travels through from the leaves to the roots (016).

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B. Animals

The literature search revealed no information relative to the use of sulfamic acid or any of its compounds in commercial animal feeds, or to their presence in animal tissues or products. However, sulfamic acid has been successfully used as a silage preservative at a level of 0.5%, final concentration (017).

C. Synthetics and Industrial Environments

1. Sulfamic acid and sulfamates are used in the papermaking industry and may be present in paper and paperboard containers used to package foods (025, 060). Their use in this connection is regulated by the Food and Drug Administration (060).

2. Sulfamic acid, by virtue of being a strong but non-corrosive acid, is used for cleaning equipment in the dairy, brewing, and sugar industries, and in meat, rabbit, poultry, egg, and vegetable processing plants (060). In some of these industries, its use is regulated by the U.S. Department of Agriculture (060,024).

3. Several preparations containing sulfamic acid or sulfamates have been developed for treating public water supplies to control objectionable taste and odor, to inhibit corrosion in the system, and to stabilize the added chlorine (047, 048, 068, 045, 034).

4. Ammonium sulfamate is widely used to flame-proof such materials as draperies and curtains for public buildings, decorative materials, circus tents, work clothes, blankets, and so forth. In fact, any fabric except cellulose acetate can be protected with this fire retardant. The fabric is dipped in a solution containing one to one and one-half pounds of salt per gallon of water, squeezed

through rollers, and dried. The treated material should contain sulfamate to the extent of 10% of its own weight (016, 020, 062).

5. As mentioned before (See this Section, A. Plants), ammonium sulfamate is used extensively for killing weeds, vines, brush, and the like (060).

6. Sulfamates are suitable anti-gelation agents for liquid soaps. Addition of 10% ammonium sulfamate in soap or in fulfonated detergent solutions is usually effective (026).

7. Sulfamic acid is used to clean or "acidize" water, oil, and gas wells (060).

8. Metals such as copper, silver, cobalt, nickel, zinc, cadmium, iron, and lead can be plated out successfully from sulfamic acid solutions. These metals can also be refined by the electroplating process (016, 010).

9. Another commercial application of sulfamic acid is in the dyeing industry. Here it is used to remove excess nitrite in diazotizations from the reaction mixture (016, 010).

10. Sulfamic acid is used sometimes in the preparation of high quality suede and other processed animal skins (016).

D. Natural Inorganic Sources

(None)

BIOLOGICAL DATA

I. Acute Toxicity

A. Mice

Data from an acute toxicity test with nickel (II) sulfamate, performed by the Sloan-Kettering Institute for Cancer Research, were included in a summary of biological tests reported by the Chemical-Biological Coordination Center, National Research Council (014). This test was performed according to Sloan-Kettering's routine procedure for screening compounds for the Sarcoma 180 assay.

Adult mice, 3 to 5 per group, were given single injections of nickel (II) sulfamate intraperitoneally in doses ranging from 31.3 to 500 mg/kg BW. The solvent used was isotonic saline. The animals were then observed for signs of toxicity over a period of seven days. Time of death was recorded for all fatalities.

At the 500 mg/kg level, all of the mice died: one within five minutes, three within 15 minutes. The fifth mouse did not succumb until the third day. The animals exhibited dyspnea and straining prior to death.

At the 250 mg/kg level, two of three mice died on the third day; the other animal survived the entire test period of seven days.

There were no deaths at the lower dose levels. The data are summarized in Tables 1 and 4.

Table 1. Acute Toxicity of Sulfamic Acid and Some of its Salts

Substance	Animal	Sex & No.	Route	Dosage mg/kg body wt.	Measurement $(LD_{50}, ED_{50}$ or other)	Ref. Bibliogr. No.
Sulfamic acid	white rat	28 males	p.o.	1600	MFD[a]	Ambrose (002)
Sulfamic acid	rat	----	p.o.	1600	MLD	Merck Index (062)
Sulfamic acid	white rat	20 males	i.p.	<100	MFD	Ambrose (002)
Ammonium sulfamate	white rat	18 males	p.o.	>1600	MFD	Ambrose (002)
Ammate[d]	rat	----	p.o.	3900	LD_{50}	Lehman (040)
Ammonium sulfamate	white rat	34 males	i.p.	800	MFD[b]	Ambrose (002)
Nickel (II) sulfamate	mouse (adult)	17 males	i.p.	250	LD[c]	Chem.-Biol. Coord. Ctr., NRC (014)

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[a]MFD = 25% of animals
[b]MFD = 60% of animals
[c]LD = 67% of animals
[d]Ammate, according to the Merck Index, contains a minimum of 80% ammonium sulfamate.

B. Rats

Ambrose (002) studied the acute toxic effects of sulfamic acid
and ammonium sulfamate in the rat by both oral and parenteral
routes. The results are summarized in Table 1. Details of the
tests are given below and in Tables 2 and 3.

1. In the oral toxicity test, male white rats (80-100 grams BW),
5 to 10 per group, were given sulfamic acid by stomach tube in
single doses ranging from 400 to 1600 mg/kg BW. Ammonium sulfamate
was given in the same manner to groups of 5 to 8 animals in doses
of 800 to 1600 mg/kg BW.

Two of eight animals in the sulfamic acid group at the 1600 mg/kg
level died, 12 to 20 hours after receiving the compound, without
showing any preliminary signs of toxicity. All other animals were
symptomless (See Table 2).

There were no deaths in the ammonium sulfamate groups and none
of the animals showed symptoms of poisoning (See Table 3).

2. The intraperitoneal toxicity test was conducted with rats
of the same specifications as used in the oral test. Groups of five
animals were given single injections of sulfamic acid in graded
doses of 100 to 800 mg/kg BW. Ammonium sulfamate was administered
to groups of five to ten animals in doses ranging from 100 to
1600 mg/kg BW.

With sulfamic acid, deaths occurred at all dose levels,
4 to 72 hours after injection. Again no signs of toxicity were
observed in any of the rats up to the time of death (See Table 2).

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Table 2. Acute Toxicity Data for Sulfamic Acid (002)

Animal	Sex	Number	Route	Dosage[b] mg/kg body wt.	Mortality (%)
White rats[a]	Male	8	p.o.	1600	25
White rats[a]	Male	5	p.o.	1200	0
White rats[a]	Male	5	p.o.	800	0
White rats[a]	Male	10	p.o.	400	0
White rats[a]	Male	5	i.p.	800	100
White rats[a]	Male	5	i.p.	400	60
White rats[a]	Male	5	i.p.	200	100
White rats[a]	Male	5	i.p.	100	80

[a]Body weight = 80-100 grams
[b]Single dose

Table 3. Acute Toxicity Data for Ammonium Sulfamate (002)

Animal	Sex	Number	Route	Dosage[b] mg/kg body wt.	Mortality (%)
White rats[a]	Male	8	p.o.	1600	0
White rats[a]	Male	5	p.o.	1200	0
White rats[a]	Male	5	p.o.	800	0
White rats[a]	Male	5	i.p.	1600	80
White rats[a]	Male	10	i.p.	800	60
White rats[a]	Male	9	i.p.	400	0
White rats[a]	Male	5	i.p.	200	0
White rats[a]	Male	5	i.p.	100	0

[a]Body weight = 80-100 grams
[b]Single dose

Four of five animals injected with ammonium sulfamate at the 1600 mg/kg level succumbed. Six of ten animals at the 800 mg/kg level died. The fatalities occurred within 45 minutes following injections. Increased respiration rate preceded prostration and death (See Table 3).

3. Lehman (040) reported that Ammate, an herbicide containing a minimum of 80% ammonium sulfamate, administered to rats by the oral route, had an LD_{50} of approximately 3900 mg/kg BW. The chief symptom was listlessness, which began within a few minutes following administration and continued for 24 hours (See Table 1).

With very high doses of Ammate, tremors were noted and death usually occurred within 10 minutes. Survival after 24 hours was favorable for complete recovery.

4. No details were given concerning the acute toxicity test for sulfamic acid reported in the Merck Index (062). (See Table 1).

C. Humans

According to Gleason et al. (031), sulfamic acid has a toxicity rating of 3 (moderately toxic) based on its probable lethal oral dose for man of 500-5,000 mg/kg. Ammonium sulfamate (Ammate) is rated at 2 or 3 (slightly to moderately toxic) on this basis (500 to 5,000 mg/kg or 5,000 to 15,000 mg/kg). (See Table 5).

II. Short-Term Studies

Available information is meager on both chronic and acute toxicity for the sulfamates. A review of the literature revealed that the

Table 4. Acute Toxicity Data for Nickel (II) Sulfamate (014)

Animal	Number	Route	Dosage[a] mg/kg body wt.	Mortality (%)
Mice (adult)	5	i.p.	500	100
Mice (adult)	3	i.p.	250	67
Mice (adult)	3	i.p.	125	0
Mice (adult)	3	i.p.	62.5	0
Mice (adult)	3	i.p.	31.3	0

[a]Single injection

Table 5. Toxicity Rating Chart (031)

Probable lethal dose (human)

Toxicity Rating or class	mg/kg	for 70 kg man (150 lb)
6 super toxic	less than 5	A taste (less than 7 drops)
5 extremely toxic	5-50	Between 7 drops and 1 teaspoonful)
4 very toxic	50-500	Between 1 teaspoonful and one ounce
3 moderately toxic	500-5 g/kg	Between 1 ounce and 1 pint (or 1 lb)
2 slightly toxic	5-15 g/kg	Between 1 pint and 1 quart
1 practically non-toxic	above 15 g/kg	More than 1 quart

most detailed investigation was that of Ambrose (002) who studied

the local and systemic effects of both sulfamic acid and ammonium

sulfamate in rats, rabbits, and man.

A. Rats

1. In the oral short-term study, female white rats, 30 days

of age and averaging 50 grams in weight, were employed. Four

groups, five animals per group, were fed a basic diet containing

either 1% or 2% sulfamic acid, or 1% or 2% ammonium sulfamate,

for a period of 15 weeks. A control group of the same number was

placed on the basic diet alone. (The basic diet consisted of:

yellow corn meal 72%, casein 10%, linseed oil cake meal 10%,

ground alfalfa 2%, bone ash 1.5%, sodium chloride 0.5%, Brewer's

yeast 1%, and cod liver oil 2% (U.S.P.)). Free access to food

and water was allowed at all times. The amount of food consumed

was recorded once each week, and the average drug intake per

kilogram body weight per day was calculated.

The effect of the compounds on growth was determined by

weighing the animals at weekly intervals and comparing the

average growth curves of treated and control groups. All animals

were sacrificed at the end of the feeding period, and studied

for gross anatomical changes and histopathologic alterations

in the visceral organs.

Figure 1 shows that growth was definitely inhibited by 2%

sulfamic acid or ammonium sulfamate in the diet, but not by 1%.

An apparent rather than a real effect was ruled out by the food

consumption figures. Food intake by rats on the sulfamic acid diet

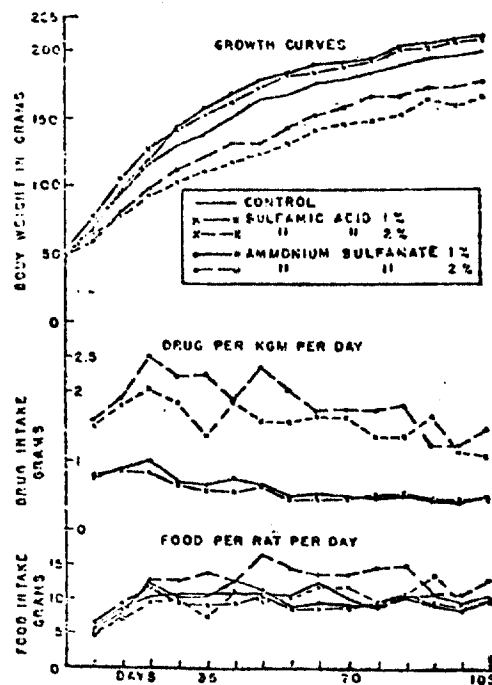was approximately the same as that of the controls, while those

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Figure 1. Average body weights, drug intake and
food consumption of white rats receiving
sulfamic acid or ammonium sulfamate in
food for 105 days. Each curve
represents an average of 5 rats. (002)

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on the ammonium sulfamate ration actually consumed more food than the control group. Ambrose concluded that the growth-inhibiting effect of sulfamic acid and ammonium sulfamate is due in part to their toxic effect and partly to a slight cathartic action which they induced.

At autopsy, no gross anatomical changes were apparent nor were histopathologic lesions evident in any of the visceral organs (See Tables 6 and 7).

2. In the second study, Ambrose (002) investigated the effect of sulfamic acid and ammonium sulfamate injected into the rat by the subcutaneous route. Ten animals (age and weight not given) were injected with 2 cc of a 4% solution of sulfamic acid or ammonium sulfamate, and then observed for signs of toxicity over a period of 30 days or more.

No deaths occurred with either of the compounds. Within 24 hours, however, sulfamic acid caused extensive necrosis at the injection site and the lesions required about a month for complete healing. In contrast, no signs of irritation, inflammation or necrosis were observed in any of the animals injected with ammonium sulfamate.

B. Rabbits

Ambrose (002) also studied the local effect of sulfamic acid and ammonium sulfamate placed in the eye of the rabbit. Five animals were used for each substance. The compounds were instilled into the conjunctival sac in the form of 0.5 ml of a 4% solution (10 mg/kg BW).

Table 6. Short-Term Toxicity Study Data for Sulfamic Acid (002)

Oral Route

| Substance | Animal and sex | Age and body wt. | Dosage[a] | | Estimated[b] mg/kg (av.) | Effect | | | |
			Number	% in diet		on food consumption	on Growth	Pathologic Gross	Microscopic
Basic diet plus Sulfamic acid	white rats (f)	30 days 50 grams (av.)	5	2	---	none	Inhibi- tion	none	none
			5	1	---	none	none	none	none
Basic diet alone			5	0	---	none	none	none	none

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[a] Fed in basic diet for 105 days
[b] See Figure 1

Table 7. Short-Term Toxicity Study Data for Ammonium Sulfamate (002)

Oral Route

Substance	Animal and sex	Age and body wt.	Dosage[a]		Estimated[b] mg/kg (av.)	Effect			
			Number	% in diet		on food consumption	on Growth	Pathologic Gross	Microscopic
Basic diet plus Ammonium sulfamate	white rats (f)	30 days	5	2	---	none	Inhibi-tion	none	none
		50 grams (av.)	5	1	---	none	none	none	none
Basic diet alone			5	0	---	none	none	none	none

---

[a] Fed in basic diet for 105 days
[b] See Figure 1

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Sulfamic acid, in the strength used, caused a moderate degree of conjunctivitis and edema. Ammonium sulfamate, on the other hand, caused no irritation.

C. Dogs

Two early preliminary studies on sulfamates in the dog have been reported.

1. Loew's colleagues (041) injected a young dog (2 kilos BW) intravenously with 700 mg/kg BW of sodium sulfamate and observed that the animal showed no ill effects.

2. A more extensive study was conducted by the Haskell Laboratory of Industrial Toxicology, E.I. Du Pont de Nemours & Co., Inc., and reported by Cupery and Gordon (020). In it, dogs fed sulfamic acid or ammonium sulfamate, 100 mg/kg BW, daily for six days manifested no symptoms of toxicity.

D. Cattle

Cottyn and Buysse (017) fed young cows (heifers) Italian ryegrass silage containing sulfamic acid in concentrations of 0.5% or 1% as a preservative. Control animals were given untreated silage of the same type and processing. Silage constituted the entire diet for all groups.

At the 1% level, the product always caused serious digestive troubles (diarrhea) which disappeared two days after the animals were put back on a diet of control silage. Another feeding of the treated material (1% sulfamic acid) would again cause severe diarrhea. On the other hand, silage containing 0.5% sulfamic acid caused no symptoms.

E. Humans

1. Cupery and Gordon (020) reported that 200 people were skin-tested with ammonium sulfamate-treated fabric (concentration in fabric not given) and no irritant effects were noted.

2. Ambrose (002) also studied the local effects of sulfamic acid and ammonium sulfamate on the skin of human volunteers. In this investigation, five subjects received applications, on the anterior surface of one arm, of a 4% solution of sulfamic acid several times daily for a period of five days. The other arm was treated in like manner with a 4% solution of ammonium sulfamate.

All volunteers experienced a slight degree of skin irritation on the arm treated with sulfamic acid and each application appeared to be more irritating than the previous one. However, the most serious reaction noted was a mere transient reddening of the skin. The area appeared normal on the following day. Ammonium sulfamate caused no skin irritation.

3. A note in the Merck Index (062) states that sulfamic acid is moderately irritating to the skin and mucous membranes, and that ammonium sulfamate may cause gastrointestinal disturbances.

4. Santmyers and Aarons (060) noted that the action of sulfamic acid on the skin is limited to the effects of its high acidity. Ammonium sulfamate is said to be neither very irritating to the skin nor very toxic; in this respect, it resembles the more common ammonium salts (chloride, sulfate).

5. According to Dupont technical literature (026), ammonium sulfamate produces irritant effects if ingested; moderate amounts, however, apparently do not cause systemic toxicity.

Sulfamic acid and its solutions cause eye injury and also irritate the nose, throat, and skin. Protective goggles are advised and precautions should be taken to avoid breathing sulfamic acid dust (025).

6. A note in the Condensed Chemical Dictionary (034) also indicates that ammonium sulfamate is moderately toxic by ingestion.

7. The Threshold Limit Value for ammonium sulfamate is 15 mg per cubic meter of air, according to the American Conference of Governmental Industrial Hygienists (1962), as reported in the Dupont Company data sheet previously mentioned (026). "This concentration in air is intended to represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect."

The Dupont article goes on to quote that, "Support for this value is presented in Documentation of Threshold Limit Values by the American Conference of Governmental Industrial Hygienists (1962) as follows:

"Ammonium sulfamate has an acute oral LD_{50} of 3900 mg/kg for
rats. It is thus improbable that acute or chronic poisoning
can result from exposure to it under ordinary conditions
of use. The Threshold Limit Value (15 mg/m^3) is assigned
by analogy in the absence of inhalation toxicity data,
and because several years of extensive use have apparently
caused no illness."

III. Long-Term Studies

No information available

IV. Special Studies

A. Humans

Conceivably, sulfamates could have an effect on the normal flora
of the gastrointestinal tract of man in the light of two studies:

1. Ortenzio, Friedl, and Stuart (054) reported that sulfamic
acid has germicidal properties in vitro.

2. Murray (047) noted that a very high dilution of zinc sulfamate
halves the amount of chlorine needed as a water disinfectant.

BIOCHEMICAL ASPECTS

I. Breakdown

Sulfamic acid is stable when dry (062). However, it slowly hydrolyzes in cold water, and more rapidly at higher temperatures, to ammonium bisulfate (NH_4HSO_4) (016, 062, 010).

Ammonium sulfamate is stable in neutral or alkaline aqueous solutions, even at temperatures as high as 100°C (062, 065). Moreover, it does not decompose on evaporation. This characteristic is important not only in its application as an herbicide but also with respect to its possible hazard as a food contaminant (berries, fruits, vegetables, etc.).

Ammonium sulfamate is apparently decomposed quite rapidly by microorganisms in the soil (041).

Cupery and Gordon (020) reported that a study on dogs, by the Haskell Laboratory of Industrial Toxicology, revealed that the sulfamate ion taken by the oral route apparently does not decompose spontaneously in the body, at least not in the dog. Both sulfamic acid and ammonium sulfamate were used in this study.

II. Absorption-Distribution

No information

III. Metabolism and Excretion

Cupery and Gordon (020) concluded that the sulfamate ion administered to the dog orally, apparently was not metabolized but was excreted unchanged in the urine.

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IV. **Effects on Enzymes and Other Biochemical Parameters**

A. Mice

In the acute toxicity study on nickel (II) sulfamate (See BIOLOGICAL DATA, I. Acute Toxicity, A. Mice), it was noted that mice given 500 mg/kg BW exhibited dyspnea (labored respiration) and straining before succumbing.

B. Rats

In the study by Ambrose, described earlier (002), the following physiologic effects of sulfamic acid and ammonium sulfamate were noted:

1. The animals injected intraperitoneally with fatal doses of ammonium sulfamate, 800-1600 mg/kg (See BIOLOGICAL DATA, I. Acute Toxicity, A. Rats, 1), manifested respiratory stimulation prior to prostration and death.

2. Female white rats fed 2% sulfamic acid or ammonium sulfamate in the diet (See BIOLOGICAL DATA, II. Short-Term Studies, A. Rats, 1):

    a. Were definitely retarded in growth

    b. Showed evidence of a slight cathartic effect.

Neither compound at the 1% level produced either of these effects.

3. In the study referred to in the preceding paragraph, Ambrose (002) pointed out that rats on the 2% ammonium sulfamate diet consumed more food than did the basic diet controls. Sulfamic acid did not have this effect. The writer did not speculate concerning the under-lying mechanism(s) involved.

C. Dogs

Ambrose (002) studied the effect of sulfamates on blood pressure and respiration in this animal. Dogs under ether anesthesia were injected intravenously with sulfamic acid or ammonium sulfamate at levels of 20 mg/kg BW and 100 mg/kg BW, and then observed for the effects of these compounds on circulation and respiratory functions.

Both compounds, at the 100 mg/kg level, brought about a slight drop in blood pressure which promptly returned to normal. Doses of 20 mg/kg had no effect.

Both sulfamic acid and ammonium sulfamate, in doses of 100 mg/kg BW, caused a slight increase in depth of respiration; it returned to normal after about a minute. Neither compound at the 20 mg/kg level affected respiration.

D. Animals, unspecified

Wolfrom, Shen, and Summers (070), in a brief report on sulfated nitrogenous polysaccharides and their anti-coagulant effects, concluded that "the sulfamic acid group was a potent contributor to anti-coagulant activity".

E. Humans

According to the Merck Index (062), ammonium sulfamate may cause gastrointestinal disturbances in man. No details are given.

V. Drug Interaction

No information is available.

VI. Consumer Exposure Information

1. Apparently the only documented consumer exposure to a GRAS sulfamate as a direct additive occurred in the City of

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Long Beach, California, in 1967, when zinc sulfamate was added
to the water supply in trace amounts as a corrosion inhibitor (047).

For several years the water in certain parts of the city had
a disagreeable taste and odor as well as visible evidence of corro-
sion. These problems originated in 1962 when the city was forced
to rely on the Colorado River for 50% or more of its supply. The
water then became extremely corrosive and also difficult to
chlorinate successfully. The result was a very heavy bacterial popu-
lation and the associated foul taste and odor.

In 1967, the city received permission from the California State
Health Department to use a corrosion inhibitor consisting of zinc
sulfamate and phosphoric acid. This agent had been developed and
successfully tested in the laboratory during a five-year study of
the problem by the local Water Department. The inhibitor was
added to the water supply initially at a dosage of 3 ppm zinc
as zinc sulfamate. After two weeks, the zinc sulfamate content
was reduced to 1 ppm and then maintained continuously at that
level for at least two years. Results of the treatment fulfilled
or exceeded expectations. The corrosion, taste, and odor pro-
blems were virtually eliminated, and surveillance by the City
Health Department indicated "no unusual incidence of gastro-
intestinal diseases or any other water-related diseases" (047, 048).

According to Murray (048), the inhibitor's sulfamate ion
functions in two beneficial ways. By combining with the free
chlorine in the water, it eliminates the latter as a corrosion
factor and at the same time produces a long-lasting oxidant and

biocide. At Long Beach, the high bacterial concentration responsible for the obnoxious taste and odor was reduced practically to zero. When sulfamate is present, higher concentrations of chlorine can be employed without giving the water a chlorinous taste. The sulfamate ion combines with chlorine to form either a monochlorosulfamate, or a dichlorosulfamate, ion depending on the amount of chlorine used:

One mole part of Cl_2 plus 1 mole part of sulfamate yields monochlorosulfamate

$$OCl^- + NH_2SO_3^- \longrightarrow NClHSO_3^- + OH^-$$
$$\text{Monochlorosulfamate}$$

Two mole parts of Cl_2 + 1 mole part of sulfamate yields dichlorosulfamate

$$2\ OCl^- + NH_2SO_3^- \longrightarrow NCl_2SO_3^- + 2\ OH^-$$
$$\text{Dichlorosulfamate}$$
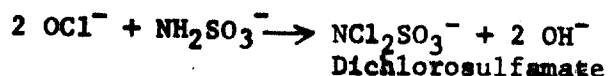
The relative advantages of the two chlorosulfamates in different situations is discussed.

When injected into the water supply, the zinc phosphate ions of the inhibitor combine to form colloidal zinc phosphate. It coats the water distribution system and "customer plumbing" with a film that protects the metal from corrosive action of dissolved oxygen, carbon dioxide, and corrosive ions. This film is so firmly deposited that it cannot be rinsed or scrubbed off. It does not become too thick, however, because colloidal zinc phosphate does not continually deposit on itself.

Victoreen's study (068) of the inhibitor confirmed Murray's findings and general conclusions. Morris and co-workers (045),

however, while agreeing in the main with Murray and Victoreen, interpret the chlorine-sulfamate chemistry somewhat differently.

The California State Health Department permits[*] the use of sulfamic acid in drinking water at a level of one part per million and enough chlorine to give a 1.5 to 2.5 ppm post-chlorine dosage (048). No information has been found as to the possible effects of long-term continuous exposure.

2. Apparently the principal consumer exposure to GRAS sulfamates in the U.S.A. results from their presence in trace amounts in paper and paperboard food containers (025, 060). However, this exposure is carefully regulated by the Federal Food and Drug Administration under Section 121.101 h: "Substances migrating to food from paper and paperboard products used in food packaging that are generally recognized as safe for their intended use, within the meaning of section 409 of the Act" (Food, Drug, and Cosmetic Act as amended, 1958) (060). The presence of sulfamates in certain types of food containers stems from their use in the paper-making industry (See CHEMICAL INFORMATION, VIII. Occurrence, C. Synthetics and Industrial Environments, 1.).

3. Certain foods represent a possible source of consumer exposure as a result of contamination with traces of sulfamic acid from its use as an acid cleaner for food processing and storage equipment (025, 060). Beer, and perhaps other beverages, should be included here also (053). (See CHEMICAN INFORMATION, VIII. Occurrence, C. Synthetics and Industrial Environments, 2.).

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[*] Use of sulfamic acid in the corrosion inhibitor was prohibited in August, 1973 (071).

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4. The review article by Santmyers and Aarons (060) gives a complete listing of the areas in industry where sulfamic acid is used as an acid cleaner. "Removing hard-water scale in food and dairy processing equipment and protein deposits on cooking and pasteurizing equipment in meat, vegetable and dairy processing plants", are typical examples. It is used also for cleaning sugar evaporators in cane-sugar and beet-sugar refineries.

5. Sulfamic acid is authorized for cleaning equipment in all departments of plants subject to "the U.S. Department of Agriculture Poultry, Meat, Rabbit, and Egg Products Inspection Programs" (025, 060).

6. Neumeister (053) investigated the value of sulfamic acid for removing beerstone from Mammuted or glass-lined tanks, kettle and open beer coolers, and stainless steel and aluminum kegs. A 2% or 3% solution removes approximately 90% of the deposit in tanks after an hour's contact, and a second application removes the remainder. For kegs, 0.2% to 2% solutions for 10 to 30 minutes suffice. Regarding a possible health hazard to consumers, Neumeister concludes that "normal rinsing should remove all of the acid, but amounts that might remain in the beer would be unlikely to affect either the beer or a consumer of it".

7. Ammonium sulfamate may be present, for a time at least, on certain fruits and vegetables that are accidentally contaminated as the substance is sprayed in adjacent areas to kill weeds or vines. In addition, food plants grown subsequently in areas cleared with this herbicide may possibly take it up from the soil. An article by Cupery and Gordon (020) contains an account of the herbicidal properties and applications of this compound. Apparently ammonium

sulfamate has several advantages over other herbicides. It does not permanently sterilize the soil, is a flame retardant rather than a fire hazard, and is regarded as non-toxic to animals. (016, 020; 041)

8. Trace amounts of sulfamic acid may be present in sugar and molasses from factories that use the sulfitation process according to a study reported by Carruthers et al. (012).

9. Liquid dentifrices represent another possible area of consumer exposure to sulfamates in view of their use as antigelation agents for soap solutions. Sulfamates were patented for this purpose in Great Britain in 1938 (035).

10. Certain lots of medicinal mineral oil could possibly contain trace amounts of sulfamic acid since it is used to acidize (clean) oil wells (060).

11. The sulfamates apparently are not used as direct food additives. None were included in a complete list of direct (non-packaging) additives submitted at a U.S. Congressional Hearing in 1971 (069). None were found in the 1972 NAS/NRC reports (051,049, 052,050). They are not listed as such in the CRC Handbook of Food Additives (028).

APPENDIX

Import Information

A considerable amount of sulfamic acid has been imported during the past few years. Figures released by the U.S. Department of Commerce show:

Jan-Feb., 1973--1,539,568 lbs.

Jan-Dec., 1972--5,271,025 lbs.

Jan-Dec., 1971--5,447,484 lbs.

Jan-Nov., 1970--9,227,371 lbs.

More detailed data are presented in Table 8 (004).

Table 8. Sulfamic Acid Imported (1970-1973).

Country	General Import		Import for Consumption	
	Net Quantity (lbs)	Value (dollars)	Net Quantity (lbs	Value (dollars)
Jan-Feb, 1973 Japan	1,539,568	146,027	Same as for General Import	
1972 Japan	5,271,025	495,609	Same as for General Import	
1971 W. Germany	125,397	12,596	69,841	6,272
Switzerland	1,230	301	1,230	301
Japan	5,320,857	449,645	5,320,857	449,645
All countries	5,447,484	462,542	5,391,928	456,218
Jan-Nov, 1970 Japan	9,142,950	646,512	9,142,550	646,512
Other countries	84,821	6,798	84,821	6,798
All countries	9,227,371	653,310	9,227,371	653,310

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STUDIES ON THE PHYSIOLOGICAL EFFECTS OF SULFAMIC ACID AND AMMONIUM SULFAMATE*

ANTHONY M. AMBROSE

From the Department of Pharmacology, University of Louisville School of Medicine, Louisville, Kentucky

RECENTLY Cupery and Gordon (1) have reviewed the properties and industrial applications of sulfamic acid and ammonium sulfamate. They also point out that very little information is available relating to the physiological properties of these compounds, other than preliminary studies by the Haskell Laboratory of Industrial Toxicology in which 1 gram daily fed to dogs for six days gave no systemic effects, and that brief contact with the skin produced no irritation.

Because of the increasing industrial applications of sulfamic acid and ammonium sulfamate, and the dearth of knowledge dealing with the toxicity of these compounds, about a year ago we were prompted in making the studies herein reported.

Sulfamic acid and ammonium sulfamate were studied with regard to their toxicity after intraperitoneal injection, oral administration, application to the skin, and the action on blood pressure and respiration. In most of these studies 4 per cent solutions of sulfamic acid or ammonium sulfamate were used. The pH of these solutions, when measured electrometrically, were 0.82 and 4.82 respectively. In studies on the continued oral administration, the compounds were mixed with the food and fed to rats ad libitum.

ACUTE TOXICITY

The acute toxicity of sulfamic acid and ammonium sulfamate was studied in male white rats weighing between 80 and 100 grams each after single intraperitoneal injection or oral administration by stomach tube. The dosage range, number of animals used, and the mortality are summarized in Table 1. All doses were administered in terms of sulfamic acid per kilogram of body weight.

Sulfamic acid after intraperitoneal injection in doses of 0.1 to 0.8 gram per kilogram produced no toxic symptoms, although deaths occurred on all these dose levels 4 to 72 hours after administration. After oral administration the minimal fatal dose (M.F.D.) killing any animal was found to be 1.6 grams per kilogram. No toxic symptoms were

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observed. Death occurred 12 to 20 hours after administration.

Ammonium sulfamate after intraperitoneal injection appeared to be definitely less toxic than sulfamic acid. The M.F.D. was found to be 0.8 gram per kilogram. Fatal doses of ammonium sulfamate produced stimulation of respiration and prostration. Death occurred within 45 minutes following administration. Rats receiving doses of as much as 1.6 grams per kilogram of ammonium sulfamate orally survived without showing toxic symptoms.

TABLE 1

ACUTE TOXICITY OF SULFAMIC ACID AND AMMONIUM SULFAMATE

DOSE	SULFAMIC ACID				AMMONIUM SULFAMATE			
	Intraperitoneal		Oral		Intraperitoneal		Oral	
	Number of animals				Number of animals			
	Used	Dead	Used	Dead	Used	Dead	Used	Dead
grams/kgm.								
0.1	5	4			5	0		
0.2	5	5			5	0		
0.4	5	3	10	0	9	0		
0.8	5	5	5	0	10	6	5	0
1.2			5	0			5	0
1.6			8	2	5	4	8	0

CHRONIC TOXICITY

The toxicity of sulfamic acid and ammonium sulfamate when added to the basic diet of rats was studied in female white rats 30 days of age and averaging 50 grams in weight. Five groups of five rats each were selected and placed in cages in groups of five. One group was placed on the basic diet consisting of yellow corn meal 72, casein 10, linseed oil cake meal 10, ground alfalfa 2, bone ash 1.5, sodium chloride 0.5, Brewer's yeast 1, and cod liver oil (U.S.P.) 2. The remaining groups were placed on two levels of sulfamic acid, 1 and 2 per cent, and two levels of ammonium sulfamate, 1 and 2 per cent. The 1 and 2 per cent

levels of ammonium sulfamate supplied the same amount of sulfamic acid as did the 1 and 2 per cent levels of sulfamic acid respectively. Free access to food and water was allowed at all times. Rats and food consumption were recorded once each week for 15 weeks, and the average weights, food consumption, and drug consumption of the animals in each group were plotted as shown in Figure 1.

From the figure it can be seen that sulfamic acid or ammonium sulfamate in 1 per cent con-
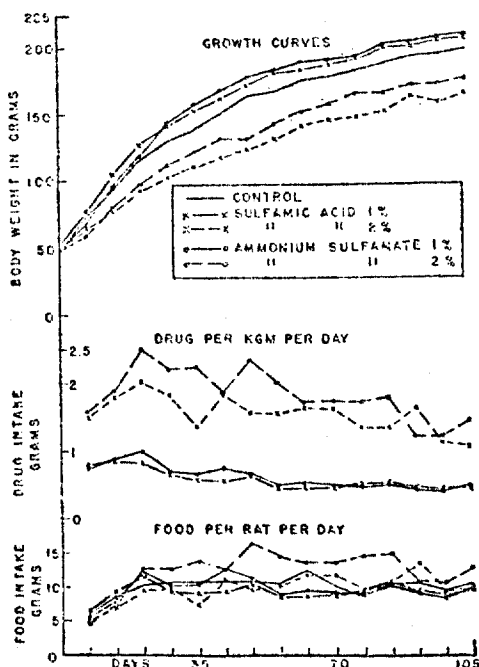

Fig. 1. Average body weights, drug intake and food consumption of white rats receiving sulfamic acid or ammonium sulfamate in food for 105 days. Each curve represents an average of 5 rats.

centration in the diet had no effect on growth rate of rats as compared to controls. Food consumption of rats on this dietary level was not significantly different from that of the controls. In rats on the diets containing 2 per cent sulfamic acid or ammonium sulfamate growth was definitely inhibited. However, the inhibition in growth rate was not due to decreased food consumption since in the group of rats on 2 per cent sulfamic acid the food intake was not significantly different from that of the controls, while in the group of rats on 2 per cent ammonium sulfamate diet, food consumption was greater than that of the controls. Therefore, the inhibition in growth rate of rats maintained on 2 per cent sulfamic acid or ammo-

nium sulfamate diets respectively, we feel was due partly to the toxic action of the compounds and partly to the slight cathartic action induced by the compounds.

At the termination of the feeding period all animals were sacrificed. Grossly no changes were apparent. Histological examination of the visceral organs failed to reveal any changes that could be ascribed to the drugs.

LOCAL EFFECTS

The local effects of sulfamic acid and ammonium sulfamate were studied on rats by subcutaneous injection, on rabbits by instillation into the conjunctival sac, and on humans by cutaneous application.

In 10 rats following the subcutaneous injections of 2 cc. of a 4 per cent solution of sulfamic acid extensive necrosis appeared at the site of injection within 24 hours, which healed completely in about 30 days. After the subcutaneous injection of 2 cc. of a 4 per cent solution of ammonium sulfamate, no signs of irritation, inflammation, or necrosis were observed.

The instillation of 0.5 cc. of a 4 per cent solution of sulfamic acid into the conjunctival sac of 5 rabbits produced a moderate degree of conjunctivitis and edema. The instillation of a similar amount of ammonium sulfamate into the conjunctival sac of 5 rabbits did not produce any irritation.

To the anterior surface of one arm of each of 5 human subjects a 4 per cent solution of sulfamic acid was applied several times a day for 5 days. The other arm was similarly treated with a 4 per cent solution of ammonium sulfamate. To the arm receiving sulfamic acid, a slight degree of irritation was experienced by all subjects. Each subsequent application appeared to be more irritating than the previous one. In some subjects a slight reddening of the skin was produced. These reactions did not appear cumulative since on the following day the treated arms appeared normal. To the arm treated with ammonium sulfamate no irritation was experienced by any of the subjects.

EFFECT ON CIRCULATION AND RESPIRATION

The effects of sulfamic acid and ammonium sulfamate after intravenous injection on blood pressure and respiration were studied in dogs under ether anesthesia. In doses of 20 mgm. per kilogram sulfamic acid or ammonium sulfamate had no

effect on either blood pressure or respiration. In doses of 100 mgm. per kilogram, both sulfamic acid and ammonium sulfamate produced a slight fall in blood pressure which promptly returned to normal. On respiration the only effect noticed was a slight increase in depth, which returned to normal after about one minute.

SUMMARY AND CONCLUSION

1. The acute toxicity of sulfamic acid and ammonium sulfamate has been determined in rats following intraperitoneal and oral administration. Sulfamic acid after intraperitoneal injection is considerably more toxic than ammonium sulfamate. After oral administration in doses of 1.6 grams per kilogram sulfamic acid was fatal to 25 per cent of the rats, while ammonium sulfamate caused no fatalities.

2. The continued oral ingestion of sulfamic acid or ammonium sulfamate to female white rats for 105 days caused an inhibition in growth rates of rats on concentrations of 2 per cent, but no effect on 1 per cent, in the diet of the respective compounds. Retardation of growth on the 2 per cent level was not due to restricted food intake, since food consumption of these animals was as great as, or greater, than that of the controls.

3. Sulfamic acid after subcutaneous injection in rats, on the conjunctiva of rabbits, and after cutaneous application on humans was definitely irritating, while ammonium sulfamate did not produce any irritation.

4. Circulation and respiration were not seriously influenced by the compounds after intravenous injection of 100 mgm. per kilogram.

5. From these studies it appears, therefore, that sulfamic acid or ammonium sulfamate presents no serious health hazards, but that sulfamic acid is definitely more toxic by all modes of administration.

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Comparison of Methods for Determination of Sulfamates

WILLIAM W. BOWLER AND ERIC A. ARNOLD

Department of Chemistry and Chemical Engineering, Case School of Applied Science, Cleveland, Ohio

The use of standard nitrite solution for the direct titration of primary amino groups has been extended to the determination of sulfamates. The titration of the acidified sulfamate solution with standard sodium nitrite, using an external indicator such as starch-iodide, yields satisfactory results on solutions of known sulfamate content. The method is compared with those in the literature.

SULFAMIC acid and many of its salts are proving to be very useful industrial chemicals for such purposes as fire retardants and weed killers (*3*). A study was recently undertaken in this laboratory on the rate of hydrolysis of sulfamic acid, and a method for determining this acid in the presence of ammonium sulfate and sulfuric acid was needed.

Because of this, it was decided to undertake a review of the methods of analysis for the sulfamate ion with a view to finding a rapid, simple, yet accurate procedure for its determination. A search of the literature revealed that only two methods have been proposed thus far.

Baumgarten and Krummacher (*1*) precipitate the sulfates as barium sulfate from a solution surrounded by ice, and filter off and weigh in the usual manner the barium sulfate produced. A second portion of the same solution is acidified with dilute hydrochloric acid and heated to boiling with an excess of sodium nitrite solution. The sulfamate ion is quantitatively oxidized to sulfate ion and free nitrogen. Barium sulfate is then precipitated, filtered, and weighed in the usual manner. In the first sample, only the sulfates are precipitated, while in the second sample, in addition to the sulfates originally present, the sulfates produced by the oxidation of the sulfamate are also precipitated. From the difference is obtained the weight of barium sulfate equivalent to the sulfamate in the original sample.

Meuwesen and Merkel (*4*) treat the sulfamate solution, acidified with dilute sulfuric acid, with excess sodium nitrite in a special evolution flask, and measure the volume of nitrogen evolved after removing the nitric oxide by bubbling the gas through alkaline permanganate. The volume of nitrogen, after correction to standard conditions, is a measure of the sulfamate in the sample analyzed.

Both methods offer disadvantages. The Baumgarten and Krummacher method is slow and tedious like all gravimetric procedures, and the Meuwesen and Merkel procedure, though rapid, is subject to all the hazards of a gas evolution method and requires special apparatus.

It was decided to attempt the direct titration of the acidified sulfamate solution with sodium nitrite, producing a simple, rapid volumetric method, similar to methods for the determination of primary amino groups. Methods of this type are given in the U. S. Pharmacopeia (*5*) for the analysis of sulfanilamide and sulfapyridine.

Cumming and Alexander (*2*) have recommended the same titration for the reverse purpose, the standardization of sodium nitrite solutions. They add sodium nitrite to the acidified sulfamic acid solution until about three fourths of the sulfamic acid has reacted. They then warm the solution to 50° C. and continue the titration slowly, using an external indicator such as starch-iodide solution or Griess' diazo reagent, a mixture of sulfanilic acid and α-naphthylamine, to determine the end point.

With this background in mind, the following procedure was adopted and found satisfactory.

One hundred milliliters of sulfamate solution containing 0.15 to 0.2 gram of sulfamic acid are acidified with 10 ml. of 10% sulfuric acid, and titrated slowly at room temperature in an Erlenmeyer or iodine flask with a standard sodium nitrite solution. The sodium nitrite solution should be approximately 0.2 N with respect to sulfamate, according to the equation

$$HNO_2 + NH_2-SO_2-OH \longrightarrow N_2 + H_2SO_4 + H_2O$$
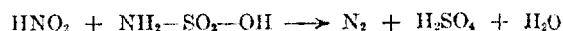
After the addition of each 5 or 10 ml. of nitrite solution the flask is stoppered and shaken vigorously to aid in the removal of the nitrogen evolved. Near the end point the titration must be carried out drop by drop, with shaking after each addition. As soon as a drop of the titrated solution causes a blue discoloration of the starch-iodide solution on a spot plate, the equivalence point is considered reached.

This procedure was tested on solutions containing known amounts of La Motte's sulfamic acid, dried to constant weight in a vacuum oven at 35°, and titrated with 0.1 N carbonate-free sodium hydroxide, using phenolphthalein as an indicator. The results are given in Table I.

It can be seen from the above data that the best concentration is 0.15 to 0.20 gram of sulfamic acid in 100 ml. of solution. The accuracy falls off if there is more than 0.25 gram in this volume. The accuracy in the very dilute solutions would probably be increased if more dilute sodium nitrite were used.

In order to make a comparison of the two previous methods with the direct titration, three commercial samples of ammonium sulfamate were analyzed by all three methods (Table II). Samples 1 and 3 were fire retardants for flameproofing fabrics, and sample

Table I. Determination of Sulfamic Acid

Sulfamic Acid Taken Gram	0.2177 N NaNO₂ Ml.	Sulfamic Acid Found Gram	Difference Gram
0.0202	2.91	0.0205	
	2.92	0.0206	
	2.94	0.0207	
	2.91	0.0205	
	Av.	0.0206	+0.0004
0.0506	7.18	0.0505	
	7.22	0.0508	
	7.24	0.0510	
	7.23	0.0509	
	Av.	0.0508	+0.0002
0.1012	14.44	0.1016	
	14.36	0.1010	
	14.38	0.1012	
	14.40	0.1013	
	Av.	0.1013	+0.0001
0.2025	28.82	0.2029	
	28.74	0.2024	
	28.76	0.2025	
	28.74	0.2024	
	Av.	0.2025	±0.0000
0.2531	35.81	0.2520	
	35.78	0.2518	
	35.91	0.2527	
	35.91	0.2527	
	Av.	0.2523	−0.0008
0.2898	40.80	0.2872	
	40.97	0.2884	
	40.99	0.2885	
	41.15	0.2896	
	40.93	0.2881	
	Av.	0.2884	−0.0014

1 mole of NaNO₂ is equivalent to 1 mole of NH₂SO₂OH; 1 ml. of 0.2177 N NaNO₂ is equivalent to 0.007045 gram of NH₂SO₂OH.

Table II. Comparison of Methods

| Method | Ammonium Sulfamate | | | (La Motte). Sulfamic Acid |
	Sample 1 %	Sample 2 %	Sample 3 %	Sample 4 %
Baumgarten and Krummacher	98.50	86.75	69.02	100.2
	98.81	86.48		
Av.	98.65	86.62		
Meuwesen and Merkel	96.5	84.0	69.5	99.8
	96.3	84.0	69.2	
Av.	96.4	84.0	69.4	
Direct titration	96.47	83.91	69.29	100.0
	96.37	84.48	68.97	
Av.	96.42	84.20	69.13	

2 was a weed killer. The purified sulfamic acid obtained from the La Motte Chemical Company is also included.

Several other methods of analysis were tried, without success. First, the sulfamate solution to be analyzed was acidified and treated with an excess of sodium nitrite. The excess nitrite over that required to react with the sulfamate was then determined by adding excess potassium permanganate, and the excess potassium permanganate was determined by either of the standard methods, using ferrous ammonium sulfate or potassium iodide and sodium thiosulfate. Instead of using potassium permanganate, an attempt was made to determine the excess nitrite directly with potassium iodide and sodium thiosulfate, carrying out the titration in an atmosphere of carbon dioxide. Neither method gave good results.

Finally, an attempt was made to find a redox indicator for the direct titration of sulfamate with nitrite. Naphthol blue-black gives a color change from blue to purple near the equivalence point, but the end point is too sensitive to pH, and the indicator blank correction too large to give satisfactory results. However, this indicator is useful in finding an approximate end point for use in conjunction with the external indicator.

Oxidizing constituents in the solution, such as ferric salts, ozone, hydrogen peroxide, and chlorine, interfere with the detection of the end point. In the presence of any of these, Griess' diazo reagent can be used instead of the starch-iodide solution.

SUMMARY

A study of methods for determining the sulfamate ion resulted in the extension of the method of titrating sulfanilamide and sulfapyridine with a standard solution of sodium nitrite, using a starch-iodide solution as an external indicator to the determination of the sulfamate ion.

Naphthol blue-black serves as an internal indicator to give an approximate end point but because of its dependence on the pH of the solution, it cannot be used for an accurate determination of end point.

The method developed is rapid, direct, and as accurate as existing methods, and requires no special apparatus.

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The SO_2 content of the stove gases at several beet-sugar factories was mostly
97-99%; the content of SO_2 (or total acidic gases) in exit gases from sulfi-
tation towers was negligible. The S content of condensates from the vapors
from evaporators was also negligible. Analyses of S in carbonatation juice,
thin juice, juice in the evaporators, and in thick juice were made as detns.
of SO_2 released by acid reflux, SO_2 released by alkali hydrolysis followed by
acid reflux, and sulfate concn. The figures for SO_2 by acid reflux varied widely
from factory to factory. No addnl. SO_2 was released by alkali hydrolysis of
thin juice, but extra amts. were obtained from thick juice. These quantities
are probably related to the amt. of invert sugar destroyed during passage
through the evaporators. The only significant increase in sulfate concn.
occurred between the 2nd carbonatation and thin juice stages; the amts. vary
considerably in different factories. The oxidn. to sulfate is not related to
the O content of tower gases (1 factory used liquid SO_2 as the gas source),
but it must occur in some reaction in soln. It was previously shown that the
S measureable by the above methods in molassses accounted for only about 50%
of the SO_2 used. Total S analyses by oxidn. with $HClO_4$ in the presence of
HNO_3 have now confirmed this and have shown that most of the SO_2 can be
measured in the molasses. Tests of color formation on heating sirups contg.
sucrose, invert sugar, $NaHCO_3$, and varying amts. of $NaSO_3$ showed that the
increase in color (after 17 hrs. at 85) was kept low by the presence of SO_2
and that the prior addn. of degradation products of invert sugar had no effect
on the final color and did not increase the sulfite requirement. Analyses of
ash from a sample of sugar of esp. high ash content showed that K salts (as
sulfate) formed 80% of the sulfated ash. A salt could be pptd. from the
sugar soln. by basic lead acetate. On decompn. of this salt with H_2S, an acid
could be crystd. which was proven to be sulfamic acid. K sulfamate does not
give a Pb salt ppt.; therefore, the sulfamic acid must be a decompn. product of
a substance in the "ash". K imidodisulfonate has previously been detected in
molasses (Veibel and Brieghel-Muller, C.A. 41, 1861a), and its presence
in molasses from various white-sugar factories which use sulfitation has now
been confirmed. The imidodisulfonate would give sulfamic acid by hydrolysis;
it can itself be formed by partial hydrolysis of the related aquoammonosulfuric
acid, nitrilosulfonic acid. It was found that the nitrilosulfonate is readily
produced when KNO_2 and potassium bisulfite solns. are mixed. Examn. of aq.
macerates of fresh beet showed that small amts. of nitrate were present. The
nitrate could be reduced to nitrite by such bacteria as Bacillus stearothermo-
philus, which occurs in diffusion systems. Conditions may, therefore, occur in
sulfitation towers such that aquo-ammonosulfuric acids are formed.

* Original article was unavailable. An abstract is reproduced here.

Gasometric Determination of Nitrite and Sulfamate

W. N. CARSON, JR., *Hanford Works, General Electric Co., Richland, Wash.*

A micromethod, suitable for the determination of small amounts of nitrite in the presence of a large amount of nitrate, and with a minimum number of manipulations of the actual sample because of radiation hazard, was required. A gasometric determination has been developed that can determine 0.01 mg. of nitrite with a precision of ±3.0% and 0.8 mg. with a precision of ±0.3%. The method is highly specific and few interferences are encountered. The entire procedure requires 20 minutes. A simple modification of the procedure allows the determination of sulfamate with a precision of ±5% for samples containing 2 mg. Interferences with the method are limited to compounds that contain the amino (—NH₂) group. The method described permits a rapid determination of nitrite and sulfamate with minimum sample manipulation. It is possible that the method could be adapted to the determination of the amino group in compounds other than sulfamate.

THIS investigation was made to develop a rapid and precise method for the determination of small quantities of nitrite in the presence of large amounts of foreign ions and diluents. A simple modification of the procedure enables a similar determination of sulfamate to be made.

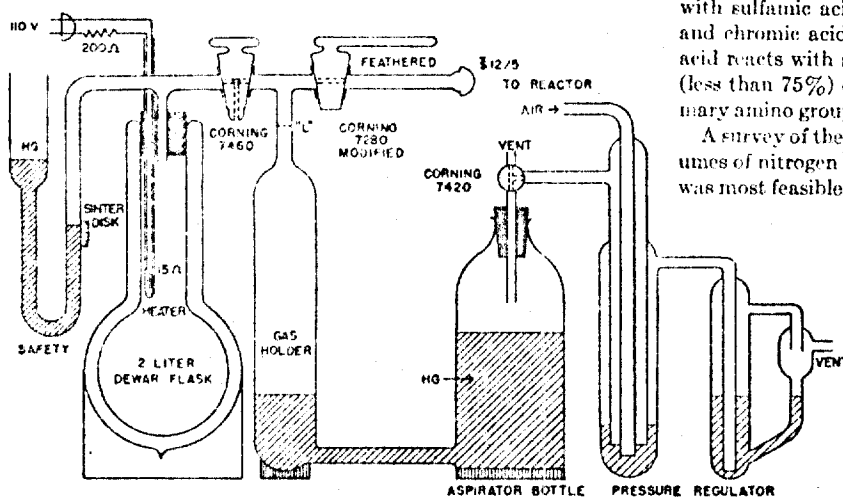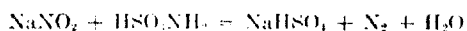The determination is based on the rapid quantitative reaction of nitrite with sulfamate in acid solution,

$$NaNO_2 + HSO_3NH_2 = NaHSO_4 + N_2 + H_2O$$

and the subsequent measurement of the volume of nitrogen evolved. This reaction is the basis for a titration method for sulfamic acid which was first suggested by Baumgarten and Morgraff (2).

Some substances which interfere with the method can exist in alkaline solution with nitrite; nitrite will oxidize or reduce these substances when the sample is acidified. Other interfering substances react with sulfamic solution in acid solution to give gases which are unabsorbable in alkali. Halogens and chlorates react with sulfamic acid to give nitrogen; permanganate, ferric iron, and chromic acid do not react (1). Concentrated (81%) nitric acid reacts with sulfamic acid to give nitrous oxide; dilute acid (less than 75%) does not react. Substances containing the primary amino group (—NH₂) react with nitrite to give nitrogen.

A survey of the apparatus that is useful for measuring small volumes of nitrogen showed that a modified micro-Dumas apparatus was most feasible. In this apparatus, the nitrogen is evolved in a reaction flask and is swept into an azotometer with a stream of pure carbon dioxide which is removed by absorption in sodium hydroxide.

Figure 1. Carbon Dioxide Generator and Gas Holder

NITRITE DETERMINATION

Apparatus. The apparatus is shown in Figures 1 to 3. The carbon dioxide generator is essentially that described by Niederl and Niederl (4), but the safety vent is modified in that a sintered-glass

disk is used in place of the filter paper assembly. In use, solid carbon dioxide is placed in the Dewar flask and the sublimed gas is kept at a sufficiently-high pressure so that gas is continually vented through this disk. The pressure is adjusted by adding or removing mercury in the safety reservoir. A pressure of 30 to 40 cm. of mercury above atmospheric pressure is used. The heater is often necessary to augment the "heat leak" of the flask in order to provide gas in the quantities needed. After the flask is flushed for 24 hours, the blank is 0.002 to 0.003 ml. per 100 ml. of gas used. One filling of dry ice is ordinarily sufficient for several weeks; however, the flask was recharged every week during this investigation. The gas holder is similar to the one described by Niederl and Niederl (4), but the mercury is manipulated with a pressure lift which may be omitted. The pressure of the incoming air is regulated by the pressure regulator to a value just sufficient to raise the mercury to level L (Figure 1), and thus mercury cannot be accidentally forced into the train. The pressure regulator is the one described by Carson (3). The adjusted capacity of the gas holder is 100 ml. The capacity is altered by varying the amount of mercury in the aspirator bottle.
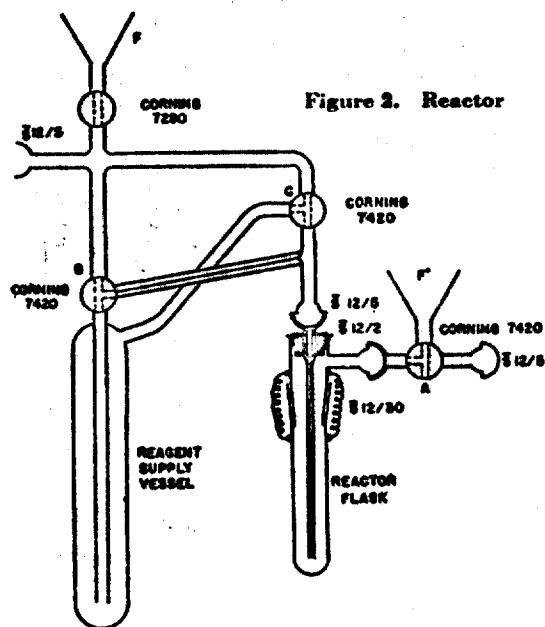

Figure 2. Reactor

The reactor design (Figure 2) permits complete outgassing of the reaction flask and reagent. Stopcock A permits back-flushing of the reaction flask head, which prevents premature reaction of the sample with any sulfamic acid splashed there during the previous determination. It also serves to shorten the train during outgassing, as the air in the reaction flask can be vented through it rather than through the entire train on the outgassing sweep. Funnel F provides a means of flushing out the reactor between samples to prevent premature reaction of the sample. The capacity of the reagent supply vessel is 60 ml. which is sufficient for a hundred or more determinations; the vessel is outgassed (once per filling) by suitable adjustment of stopcocks B and C. Reagent is added to the outgassed sample by manipulation of stopcock C so that carbon dioxide can enter the reagent supply vessel, but not the reaction flask, and stopcock B so that liquid can rise in the tube and pass into the capillary. The volume of the capillary is about 0.5 ml.; this amount of 0.1 N reagent is sufficient to decompose any sample that can be measured in the azotometer. When the capillary is full, stopcock B is turned so that carbon dioxide from the generator forces the reagent into the reactor flask.

Figure 3 gives the diagram of the microazotometer used. The measuring portion consists of a 1-mm. capillary with a scale in

millimeters attached. In use, the nitrogen collects in a large bubble at the base of the capillary. At the end of a run, this bubble is forced into the capillary by lifting the leveling bulb and opening the stopcock. The volume of the gas bubble is measured by the determination of the length of the capillary occupied. The capacity was 187.3 microliters for a 200-mm. length and the capillary was assumed to be of uniform bore. The semimicroazotometer used was the standard model available from supply houses, with a capacity of 1.5 ml. In use, the azotometers are filled with 50% potassium hydroxide and mercury in the usual manner.
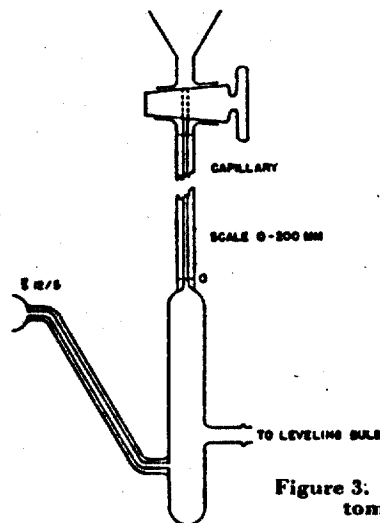

Figure 3. Microazotometer

Procedure. Use a sample of sufficient size to give a conveniently measured amount of nitrogen (0.5 to 1.2 ml. for the semimicroazotometer, 80 to 100 microliters for the microazotometer). For samples of low nitrite content, increase the size of the reaction flask to the size necessary to hold the sample. Neutralize acid solutions to alkalinity, but avoid a large excess of base. Attach the reactor flask to the apparatus, and outgas the sample with 200 ml. of carbon dioxide. If the train has been swept previously on that day, vent the gas through stopcock A and funnel F' (Figure 2). If the train has not been used that day pass the gas through the entire train, using such additional gas as necessary to remove all air. All air is removed when only microbubbles appear in the azotometer. Shut off the gas flow at the gas holder, and test the system for leaks by lowering the leveling bulb of the azotometer. A leak will appear as a continuous stream of bubbles. A few bubbles will appear when the bulb is first lowered but will not continue if the apparatus is gas tight.
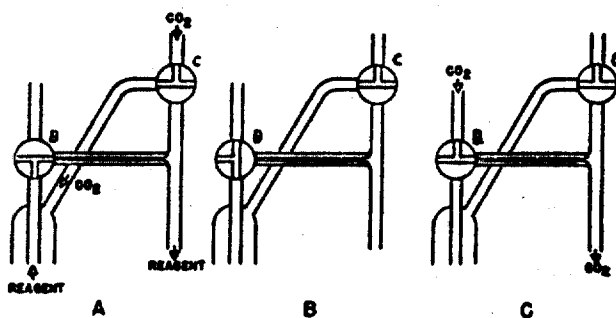

Figure 4. Position of Stopcocks during Manipulations

Introduce the sulfamic reagent (0.1 N sulfuric acid + 0.1 N sulfamic acid) as follows: (Figure 4 gives the position of the stopcocks of the reactor during this step in the determination. Part A shows the position while the capillary is being filled; part B shows the position after it is filled.) Fill the gas holder, and bring the gas in it to the pressure of the pressure regulator by manipulation of the air-lift stopcock. Heat the solution in the reaction flask by raising a large test tube filled with water at the

Table I. Determination of Nitrite

	Nitrite Added, Grams/Liter	
	4.399[a]	0.593[b]
	Nitrite found, grams/liter	
	4.407	0.600
	4.389	0.621
	4.389	0.610
	4.382	0.610
	4.371	0.621
	4.389	0.597
	4.362	0.574
	4.388	0.617
	4.405	...
	4.397	...
	4.396	...
	4.407	...
	4.403	...
	4.391	0.603
Average		
Standard deviation		
Grams/liter	±0.013	±0.018
Per cent	±0.31	±3.0

[a] Approximate volume nitrogen collected, 0.50 ml.
[b] Approximate volume nitrogen collected, 0.070 ml.

boiling point (but not actually boiling) around the reaction flask. Cautiously open stopcock B (Figure 4) to the position in part C, and allow the reagent to enter the reaction flask. Turn stopcock B back to the position in B (Figure 4) and heat the reactor flask again. Now allow just sufficient carbon dioxide to pass into the reaction vessel so that the cooling of the reactor contents does not cause a partial vacuum. Allow to cool for 1 minute, and adjust the gas flow from the gas holder to a rate such that 1 bubble of gas per second enters the azotometer. It is imperative that this rate be low, or undesirably large bubbles of nitrogen will be formed in the azotometer. When most of the nitrogen has passed into the azotometer as shown by the decreased bubble size, increase the sweeping rate to approximately 0.2 ml. per second, until the gas holder is three fourths empty, at which time increase the rate to 0.5 ml. per second. Use only one gas holder full of carbon dioxide to sweep. Raise the azotometer bulb, open stopcock A (Figure 2) to vent, and remove the sample flask. Flush out the reactor by setting the stopcocks of the reactor so that water cannot enter the reagent supply vessel, and adding water to both funnels (F and F', Figure 2); allow to rinse thoroughly. Place the next sample flask on the reactor, and outgas as outlined above. During the sweep adjust the leveling bulb of the azotometer, obtain the reading of the volume of gas, and note the temperature and pressure. Remove the nitrogen by opening the stopcock and raising the leveling bulb. At the end of each day, remove the azotometer from the train, and remove the leveling bulb and tubing. Allow the bulb and tubing to drain but do not rinse. If the tubing is rinsed, the dilute alkali formed attacks the rubber and causes the appearance of a marked discoloration in the next day's alkali. Thoroughly rinse the azotometer and remove the stopcock. Do not replace the stopcock until just before use to prevent sticking. It must be heavily greased, preferably with white vaseline.

Calculations. To compute the grams per liter of nitrite, the following formula is used:

$$\text{Nitrite (grams/liter)} = \frac{T_0 \times (P - c)}{(V - b) \times T \times P_0} \times m \times \frac{NO_2}{N_2} \times \frac{10^6}{S} \quad (1)$$

where V = observed volume of nitrogen in ml.
P = observed pressure of nitrogen in mm. of mercury
T = observed temperature of nitrogen in ° K.
b = correction to volume of nitrogen contributed by calibration of azotometer, adhesion of alkali on wall, and blank of nitrogen in carbon dioxide
c = correction to barometric pressure contributed by aqueous tension above the alkali, and barometer corrections (brass scale, etc.)
m = mass of 1 ml. of nitrogen at 0° C. and 760 mm. of mercury = 1.2505 mg. per ml.
$\frac{NO_2}{N_2}$ = factor for nitrite in nitrogen = 1.6422
S = sample size in microliters
T_0 = 273.1° K.
P_0 = 760 mm. of mercury

After substitution for the constants, the formula reduces to,

$$\text{Nitrite (grams/liter)} = 737.9 \frac{(V - b)(P - c)}{S(273.1 + t)} \quad (2)$$

where t = observed temperature in ° C.

Values for some of the corrections can be found in Niederl and Niederl (5) (aqueous tension and adsorption of alkali on the wall). Barometer corrections are obtainable from standard handbooks. The other corrections are experimentally determined. The blank should be determined by performing an actual run without a sample. It is advisable not to "zero" the azotometer for this determination because the volume of the blank is so small, but to lower the level of the alkali in the azotometer to a convenient mark, read the azotometer, run the blank, and determine the blank value by difference. It is important that gas from the generator be vented at all times through the safety valve, as otherwise the quantity in the gas holder will vary.

Results. Two standard solutions of sodium nitrite standardized by titration with permanganate were analyzed by the method described herein. The sample size taken was 202.0 microliters. The results obtained are given in Table I.

SULFAMATE DETERMINATION

Preliminary Investigation. The reaction of sulfamate and nitrite to give nitrogen can be used to determine sulfamate as well as nitrite. A difficulty arises because the final reaction mixture is an acid solution of nitrite, which on prolonged sweeping with inert gas evolves variable quantities of nitric oxide which is nonabsorbable in alkali. Consequently, an absorption section for nitric oxide removal must be added to the apparatus.
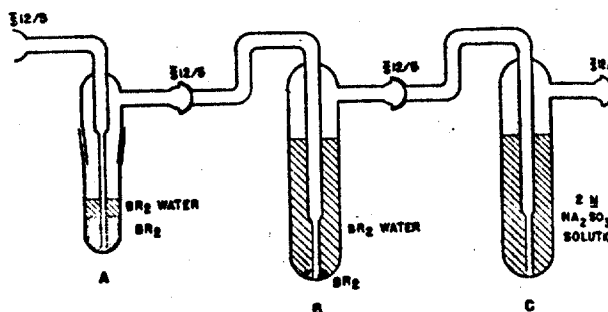

Figure 5. Nitric Oxide Scrubbing System

The common reagents in gas analysis for removal of nitric oxide are ferrous sulfate in dilute sulfuric acid and acid permanganate. Tests with numerous types of scrubbers showed neither of the reagents to be effective under the conditions of the determination. Other oxidizing agents were tried; hypochlorite and hypobromite were unsatisfactory because both gave oxygen when treated with carbon dioxide, and ammonium hexanitratocerate was unsatisfactory when the sweeping rate was above 50 ml. per hour.

The scrubbing system adopted is based on the reaction of bromine with nitric oxide in the presence of water:

$$2NO + 3Br_2 + 4H_2O \longrightarrow 2HNO_3 + 6HBr$$
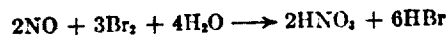
The scrubber system saturates the gas stream with bromine and water vapor. This combination gives efficient scrubbing. Bromine vapor reacts with the mercury in the azotometer; thus it must be removed from the gas stream. The best reagent for this purpose was 2 M sodium sulfite. Acid sulfites would give more capacity, but they evolve sulfur dioxide which, although readily absorbed by the 50% potassium hydroxide in the azotometer, forms the relatively insoluble potassium sulfite, which clogs the azotometer.

Apparatus. Figure 5 gives the design and details of the scrubbers. Scrubber A contains liquid bromine below a water layer and saturates the gas stream with bromine and water vapor. Scrubber B is used to prolong the scrubbing and contains bromine water. Scrubber C holds the sodium sulfite solution used to remove bromine vapor.

The remainder of the apparatus used is identical with that used

in the determination of nitrite, except that the reagent vessel is now filled with 5% sodium nitrite. The scrubbers are inserted in the train between stopcock A (Figure 2) and the azotometer.

Procedure. The sample is added to the reactor flask and acidified strongly with sulfuric acid. The procedure from this point on is identical with that for nitrite.

Calculations. The value of the sulfate is given by a formula analogous to that used to compute nitrite except for the factor $\frac{NH_2SO_3}{N_2}$ (factor for sulfamate in nitrogen).

$$\text{Sulfamate (grams/liter)} = 1541.2 \times \frac{(V - b)(P - c)}{(S)(273.1 + t)} \quad (3)$$

Results. Table II gives the results of the determination of standard sulfamate solution. These solutions were made from primary standard sulfamic acid and triple distilled water and were checked by titration against base. The sample size used was 190.9 microliters.

DISCUSSION

Although no work has been done on the adaptation of the method for sulfamate to the determination of other substances containing an amino (—NH$_2$) group, it is probable that this could be done. Conversely, substances containing these groups are the only known interference with the sulfamate method.

The apparatus described has proved serviceable. Breakage in use has been confined to the capillary extending into the sample reactor flask which has been made easily replaceable. Determination of the correct blank for use with the microazotometer is difficult to obtain directly. However, if a number of standard samples, say 5, is run, the average blank can be determined with fair precision. This indirect method is much more precise than the direct method and is more easily performed. Nitrite samples are neutralized to minimize decomposition in the outgassing sweep. This neutralization is not critical, but should be carefully done so that a large excess of alkali is avoided. The reaction mixture must be acid for the reaction between nitrite and sulfamate to proceed, and if a large excess of base is used on the preliminary neutralization, the acid normally added may not be sufficient. Additional reagent can be added, however, if necessary.

Table II. Determination of Sulfamate

	Sulfamate Added, Grams/Liter	
	7.14	10.66
	Sulfamate found, grams/liter	
	7.20	10.40
	7.21	10.84
	7.14	10.63
		10.27
		10.88
		10.75
		10.75
Average	7.17	10.70
Standard deviation		
Grams/liter	...	±0.20
Per cent	...	±1.87

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(1) Audrieth, Sveda, Sisler, and Butler, *Chem. Revs.*, **26**, 49 (1940).
(2) Baumgarten and Margraff, *Ber.*, **63**, 1019 (1930).
(3) Carson, ANAL. CHEM., **21**, 316 (1949).
(4) Niederl and Niederl, "Organic Quantitative Analysis," New York, John Wiley & Sons, 1942.
(5) *Ibid.*, p. 95.

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Chem. - Biol. Coordination Center, National Research Council, 4(5):320, 1952

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TOXICITY TESTS   (Continued)

| CBC No.	Name and Structure	Conc.	Mortality	Day of Death
505,911 (61)	Lactamide, N,N-didecyl- $CH_3CHOHCON[(CH_2)_9CH_3]_2$	*500 cmm/kg 250 125 62.5 * hyperexcitable Solvent: peanut oil	3/5 0/3 0/3 0/3	2,3,3
000,956 (68)	Mercury, diisopropyl- $(CH_3)_2CHHgCH(CH_3)_2$	500 cmm/kg 250 125 62.5 31.3 15.6 7.8 7.8 3.9 1.9 0.95 0.48 Solvent: peanut oil	3/3 3/3 3/3 3/3 3/3 3/3 3/3 1/3 0/3 0/3 0/3 0/3	1 1/2 hrs. (3) 1 1/2 hrs. (3) 1 1/2 hrs. (2); 2 1/2 hrs. (1) 1,1,1 2,3,3 2,2,2 3,3,3 3
000,957 (68)	Mercury, dipropyl- $(CH_3CH_2CH_2)_2Hg$	500 cmm/kg 250 125 62.5 31.3 15.6 7.8 3.9 1.9 Solvent: peanut oil	3/3 3/3 3/3 3/3 3/3 3/3 3/3 1/3 1/3	20 min. (3) 1/2 hr. (2); 45 min. (1) 1/2 hr. (1); 45 min. (2) 45 min. (1); 1 hr. (2) 1 1/2 hrs. (3) 1,1,1 1,2,2 1 6
X00,402 (29)	Nickel(II) sulfamate $(H_2NSO_3)_2Ni$	*500 mg/kg 250 125 62.5 31.3 * Exhibited dyspnea; straining Solvent: isotonic saline	5/5 2/3 0/3 0/3 0/3	5 min. (1) 15 min. (3); 3 3,3

Sulfamic Acid and Its Uses[1]

LEALLYN B. CLAPP

Brown University, Providence, Rhode Island

SULFAMIC acid, $HOSO_2NH_2$, has received consider-able attention since it became available in this coun-try in 1938. The ammonium salt is being sold to kill poison ivy and to flameproof cloth and paper. The acid may be used in the laboratory to prepare nitrous oxide and as a primary standard. Although it is closely related to sulfuric acid, it is a solid with a defi-nite melting point. This makes sulfamic acid unique among the strong inorganic acids. Sulfamic acid is sulfuric acid in which an —OH group has been replaced by —NH₂.

Sulfuric acid   Sulfamic acid
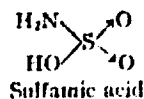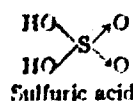
Commercially the acid is prepared from urea and fuming sulfuric acid. Although the equations do not tell the whole story, the reactions may be represented as follows:

Urea disulfonic acid
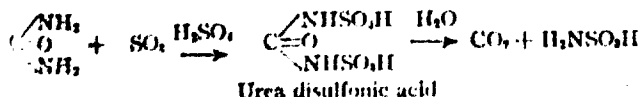
PHYSICAL PROPERTIES

Sulfamic acid is a white, non-hygroscopic solid which melts at 305°C. and is stable up to 260°C. It forms colorless compact prisms and tablets from cold solu-tion and lozenge-shaped plates on cooling a hot aque-ous solution. The crystal form as designated by Bry-ant[2] is orthorhombic bipyramidal.

Large crystals may be grown from saturated solu-tions. This may most easily be accomplished by allowing a saturated solution to stand in a desic-cator over a mild dehydrating agent such as calcium chloride. The top edge of the container is coated with paraffin to prevent creeping.

The acid is soluble in water to the extent of 24.2 g. per 100 g. of water at 25°C. It is soluble in form-amide, slightly soluble in ether, acetone, methanol, and concentrated sulfuric acid. In 70 per cent sul-furic acid, it is almost completely insoluble. It may be purified by recrystallization from water; 125 g. are dissolved in 200 g. of water preheated to 70°C. The solution is filtered three times with consequent lower-ing in temperature, and each time the material crystal-lizing from solution (altogether about 25 g.) is discarded. The final filtrate is cooled rapidly in an ice-salt mixture

and allowed to stand for 20 minutes. The crystals are removed by suction filtration, washed once with ice water, twice with cold alcohol, and finally with ether. After drying in air for an hour, they are stored in a desiccator. This product is suitable for a standard in acidimetry.[2]

CHEMICAL PROPERTIES

1. Strong Acid. Sulfamic acid is about as strong an acid as hydrochloric, nitric, or sulfuric. It is a strong acid in both aqueous solution and anhydrous liquid ammonia. The fact that it contains both labile and non-ionizable hydrogens might well be used as a teaching device for the Brønsted concept of an acid. In water sulfamic acid loses a single proton from the oxygen atom whereas the hydrogens attached to the nitrogen are firmly bound and do not break away.
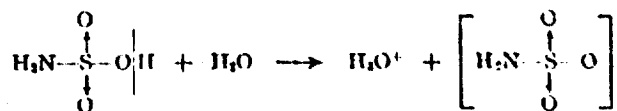

In liquid ammonia, on the other hand, two protons are easily donated to ammonia molecules, but the third hydrogen still remains firmly bound to the nitrogen.
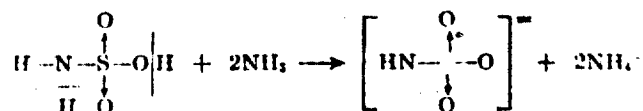
The evidence for the second stage in the ionization in ammonia is that sodium reacts with sulfamic acid in liquid ammonia to give the disodium salt, $NaNHSO_2$-ONa. Beginning students often get the idea from the ordinary mineral acids that the presence of hydrogen on the front end of a formula is all that is necessary to make an acid. Here is a chance to point out that the ease of removal of the proton depends on the kind of atom to which it is attached as well as on the solvent with which it reacts.

2. Hydrolysis. The acid is slowly hydrolyzed in aqueous solution to ammonium acid sulfate.
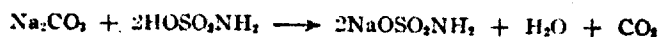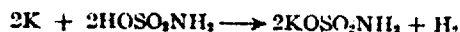
$$H_2NSO_3H + H_2O \longrightarrow NH_4HSO_4$$
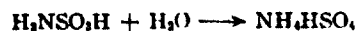
At 80°C., it is about 40 per cent hydrolyzed in six hours in 10 and 30 per cent solutions and about 25 per cent hydrolyzed in one per cent solution in the same time. In neutral or alkaline solution, sulfamic acid may be boiled without appreciable hydrolysis. As noted above, when it is recrystallized from water, the temperature should not exceed 70°C.

[1] Abstract of an address presented at the 4th Summer Confer-ence of the N.E.A.C.T., University of New Hampshire, Dur-ham, N. H., August 12, 1942.
[2] BRYANT, *J. Am. Chem. Soc.*, **61**, 2551 (1939).
[2] BUTLER, SMITH, AND AUDRIETH, *Ind. Eng. Chem., Anal. Ed.*, **10**, 691 (1938).

3. Salt Formation. Metals, metallic oxides, and carbonates are attacked by sulfamic acid to give the corresponding sulfamate.

$$2K + 2HOSO_2NH_2 \longrightarrow 2KOSO_2NH_2 + H_2$$

$$MgO + 2HOSO_2NH_2 \longrightarrow Mg(OSO_2NH_2)_2 + H_2O$$

$$Na_2CO_3 + 2HOSO_2NH_2 \longrightarrow 2NaOSO_2NH_2 + H_2O + CO_2$$

All known salts of sulfamic acid are soluble in water except the basic mercury salt. The calcium, lead, and barium salts are very soluble in water in contrast to the corresponding sulfates. Lead sulfamate is soluble to the extent of 218 grams per 100 grams of water at 25°C. This means that it is much more soluble than lead nitrate or lead acetate.

4. Reaction with Nitrous Acid. Nitrous acid reacts quantitatively with the amino group in sulfamic acid to liberate nitrogen. This is used to remove excess nitrites rapidly and effectively in diazotizations in the dye industry.

$$HOSO_2NH_2 + HONO \longrightarrow H_2SO_4 + N_2 + H_2O$$
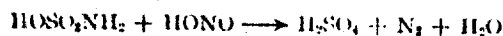
5. Preparation of Nitrous Oxide. With nitric acid, pure nitrous oxide may be prepared. This makes a good lecture demonstration without the danger of overheating which is a hazard with ammonium nitrate. By dissolving sulfamic acid in water, adding an equivalent of concentrated nitric acid and then heating the solution slowly, a smooth flow of bubbles of nitrous oxide may be obtained.

$$HOSO_2NH_2 + HONO_2 \longrightarrow H_2SO_4 + N_2O + H_2O$$

6. Oxidizing Agents. Sulfamic acid is oxidized to sulfuric acid and nitrogen according to the following equation:

$$2HOSO_2NH_2 + 3(O) \longrightarrow N_2 + 2H_2SO_4 + H_2O$$
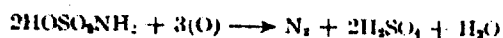
Chlorine, bromine, and potassium chlorate will effect this oxidation but chromic acid and potassium permanganate will not.

USES

1. Weed Killer. Ammonium sulfamate has been widely heralded as a killer of poison ivy. It is also effective in killing poison oak, choke cherry, hoary cress, ragweed, and Canadian thistle. It is much more effective than sodium chloride, calcium chloride, ammonium thiocyanate, and ammonium sulfate. It is as effective as sodium chlorate in all cases and better with some weeds. In addition, it is a fire retardant rather than a fire hazard. It is non-toxic to animals. For example, dogs have been given one gram per day for several days without showing systemic poisoning. The best treatment for poison ivy is a spray containing one pound of ammonium sulfamate per gallon of water. The leaves are sprayed during the late summer or early fall while still green and preferably in humid weather. The plant is killed by translocation of the salt from the leaves to the roots. Another advantage of ammonium sulfamate over some other herbicides is that it does not permanently sterilize the soil. In fact after one season,

some nitrogen will be available for plant growth from the weed killer.

2. Flameproofing Textiles. Compatibility with cellulose, as well as its fire-retardant properties, make ammonium sulfamate useful in flameproofing textiles and paper. It is especially useful for curtains and draperies in such places as theaters. Retention of the salt to the extent of 10 per cent of its own weight is enough to flameproof fabrics or paper. It may be used on any fabric except cellulose acetate and may be dry cleaned but not washed. It is easily applied by a dipping process similar to starching clothes, using one to one and one-half pounds per gallon of water. Then the cloth is squeezed through rollers and dried. Fabrics so treated will char but not burn and most of them will have no afterglow. The appearance and "feel" of the cloth are unaltered.

3. Nitrite Removal. Sulfamic acid, as has been mentioned above, reacts quantitatively with a nitrite to liberate nitrogen. This reaction has found application in the dye industry in diazotizations for the removal of excess nitrite from the reaction mixture. It is better than urea for this purpose. For example, in one process the amount of sulfamic acid used is less than one-sixth that of the urea needed and the time is cut from three hours to five minutes.

4. Tanning. In processing skins, the use of sulfamic acid in place of sulfuric has been found to give a finer and silkier grain. Another advantage which sulfamic acid possesses is that its calcium salt is soluble in water, so the acid may be used in the deliming process without leaving the lime spots which sometimes occur with sulfuric acid. Goat skin tanned with formaldehyde is said to give a tighter skin and to make a better suede when some sulfamic acid is used in the process.

5. Refining Metals. Metals like copper, silver, cobalt, nickel, zinc, cadmium, iron, and lead may be plated out successfully from sulfamic acid solution. The current densities and other conditions for best plating baths have been worked out fairly well. Solutions of lead sulfamate may some day be used for refining lead in place of the Betts process. Sulfamic acid is certainly easier to handle than fluosilicic acid and ceramic containers may be used with it.

6. Laboratory Reagent.

(a) Primary Standard Acid. Because sulfamic acid is a strong acid, is easy to purify by recrystallization from water, and is a stable, non-hygroscopic solid, it has been advocated as a primary standard acid. It is as good as potassium hydrogen phthalate, potassium acid iodate, succinic acid, and benzoic acid. Of these only potassium acid iodate is a strong acid and both it and sulfamic acid may be titrated with indicators of pH ranging from 4.5 to 9.0. Sulfamic acid, however, is cheaper than potassium acid iodate.

(b) Determination of Nitrite. Sulfamic acid may not only be used to determine nitrite but may also be used to liberate nitrite nitrogen from water before analysis of the water for dissolved oxygen.

APRIL, 1943

(c) *Preparation of Dry Nitrous Oxide.* (See above.)

(d) *Separation of Rare Earth Subgroups.* The lanthanum rare earth group may be separated from the yttrium earths by using sulfamic acid. Upon adding sodium nitrite to a cold solution of rare earth sulfamates in sulfamic acid solution the alkali double sulfates of the lanthanum group precipitate first.[1]

ACKNOWLEDGMENT

[1] KLEINBERG, TARBEL, AND AUDRIETH, *Ind. Eng. Chem., Anal. Ed.,* 11, 368 (1939).

[2] CUPERY, *Ind. Eng. Chem.,* 30, 627 (1938). GORDON AND CUPERY, *ibid.,* 31, 1237 (1939); *ibid.,* 34, 792 (1942).

THE VALUE OF AMIDOSULPHONIC ACID AS A SILAGE PRESERVATIVE

BY B.G. COTTYN AND F.X. BUYSSE

Summary

In a series of experiments on silage of Italian ryegrass, we have studied the value of amidosulphonic acid as a preservative. Amidosulphonic acid, the mono-amine of sulphuric acid (NH_2SO_3H), is a non-volatile, non-hygroscopic crystalline product with strong acid characteristics. The preservative was added in two different concentrations of 0.5% and 1% to chopped and unchopped silage. For each of the treatments we used 6 cylindrical experimental concrete silos, filled on the average with 1300 kg of chopped grass and 1000 kg of unchopped grass. Two of the experimental silos were used as controls without any additive, in two others amidosulphonic acid was added in a concentration of 0.5%, and in the last two, it was added in a concentration of 1% (see the experimental plan in Table 1).

According to various quality criteria, it appears that all objectives were at least minimumally attained; the pH was always less than 4.2 and was accompanied by a corresponding high lactic acid content in all the silos.

The percentage of butyric acid was insignificant in the chopped silage and amounted to an average of 33% in the unchopped silage. The preservative clearly had a favorable effect on the weight losses as well as on the losses of dry matter.

The relatively high percentage of azote of the preservative (14.3%) can perhaps be a valuable N source for the ruminant.

The feeding of silage to which was added 1% concentration of amido-

sulphonic acid caused serious digestive troubles (diarrhea) in the cattle. The silage with the 0.5% concentration of this product was well tolerated by the animals.

1. Introduction

The group of products used with the most success in silage of various green fodders has a base of strong mineral acids. (Virtanen, 1947) The rapid fall in pH caused by the addition of strong acids, favorably enhances the fermentation process. In this situation with the degree of increased acidity thus obtained (pH 4.2), only the bacteria of lactic acid are in favorable conditions for growth, while the bacteria of butyric acid and proteolytic micro-organisms are inhibited in their growth. Strong mineral acids in the liquid state, such as H_2SO_4, HCl and phosphoric acid (fossilan), or less strong organic acid in sufficient concentrations such as formic acid, are effective for obtaining optimum pH. The inherent dangers of handling these strongly corrosive liquids, has given rise to an expanded market of additives. Some of these are powders in which the strong acids are dispersed (such as Protosil), with a base of phosphoric acid, molasses and peat moss (Cottyn, et al., 1969), or some having strong acids in crystalline form, or some are chemical products whose effect takes place at the time of ensilage.

Monosulfonic acid, or the mono-amine of sulphuric acid, with the formula NH_2SO_3H is non-volatile, non-hygroscopic crystalline product with strong acid characteristics. The aqueous solutions have a degree of acidity comparable to that of a solution of H_2SO4 or HCl of average concentrations. It is thus an aqueous solution of amido-sulfonic acid of 1% concentration, having a pH of 1.18. The product has no specific toxicity, and even its handling produces no permanent irritating effect worth mentioning.

With the aim of studying the value of amidosulphonic acid as a preservative, we conducted a series of experiments on silage of Italian ryegrass. The product was added to the fodder, chopped and unchopped, in concentrations of 0.5% and 1%.

2. Experimental Material and Techniques Used

The green fodder used was from the first cutting of Italian ryegrass. It was ensiled in 12 small cylindrical experimental silos of concrete, containing on the average, 1300 kg of chopped fodder and 1000 kg of unchopped material. Out of the 6 experimental silos used for each treatment --- with chopped and unchopped fodder --- there was each time two control silos without preservative, two others with amidosulphonic acid in a concentration of 0.5% and the last two with concentrations of 1% of this same acid.

Table 1 shows the plan of the experiments.

TABLE 1. — Planned silage experiments (Italian ryegrass).

Ensiled material (kg)	Number of silo's	Treatment (*)	Type	Amount ·%
			Additive	
2 600	2	H	aucun-(témoin) no-(control)	
2 600	2	H	NH_2SO_3H	0,5 %
2 530	2	H	NH_2SO_3H	1 %
2 000	2	N.H.	aucun-(témoin) no-(control)	
2 000	2	N.H.	NH_2SO_3H	0,5 %
2 000	2	N.H.	NH_2SO_3H	1 %

(*) H = haché (chopped) ; N.H. = non haché (no chopped).

After the silos were filled, the fodder was covered with a plastic
sheet and put on a bed of 30 cm of soil. The silos were covered with
individual roofs of zinc to prevent the penetration of rainwater.
The whole group of the experimental silos was equipped with an open
drain which was closed after 14 days.

When the fodder was taken out of the silos it was immediately given
to a group of heiffers and was the only constituent of their diet.

The chemical composition of the fresh fodder (chopped and unchopped)
and from the different silos, obtained with and without preservative, is
shown in Table 2. By means of material taken by hand randomly from different
parts of the fresh fodder, we made up an average sampling for each silo.
For the fresh fodder, only the average composition of the chopped and
unchopped fodder is shown in the table. For the ensiled fodder, the
table shows an analysis of the average results obtained (2 silos).

TABLE 2. — Chemical composition of the fresh and ensiled Italian ryegrass.

Roughage	Type and amount of additive	Number of silo's	Treatment (*)	Dry matter (%)	Composition of the dry matter %			
					Crude protein	Digestible crude protein	True protein	Digestible true protein
Ray-grass d'Italie (produit frais) Italian ryegrass (fresh material)	—		H	16,38	12,36	8,97	10,98	7,57
Ensilage Silage	aucun-(témoin) no-(control)	2	H	16,28	12,96	10,44	6,33	3,75
	NH₃SO₃H 0,5 %	2	H	17,89	14,98	12,97	5,09	3,02
	NH₃SO₃H 1 %	2	H	19,31	15,33	12,89	6,68	4,25
Ray-grass d'Italie (produit frais) Italian ryegrass (fresh material)	—		N.H.	18,13	11,42	9,19	9,59	7,32
Ensilage Silage	aucun-(témoin) no-(control)	2	N.H.	17,62	14,19	11,01	7,72	4,54
	NH₃SO₃H 0,5 %	2	N.H.	19,50	13,85	11,44	6,51	4,15
	NH₃SO₃H 1 %	2	N.H.	19,42	16,07	13,03	7,21	4,17

(*) H = hâché (chopped) ; N.H. = non hâché (no chopped).

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It appears from Table 2 that after silage, of the chopped as well as the unchopped fodder, the percentage of crude protein as well as the percentage of digestible crude protein in dry material has increased. The increase is greater in the silos in which preservative was added than in the control silos: in general, it is most significant in the silos where the preservative was the most concentrated. These increases are explained by the percentage of N in the preservative.

By contrast, the percentage of true protein and digestible true protein decreased after ensilage in the chopped as well as the unchopped material; the decrease is greatest in the silos to which a 0.5% concentration was added.

It is clear that the progressive increase in proteins as the dosage of the preservative is increased, is essentially due to the addition of azote contained in the preservative. The percentage of N in the preserva- tive is actually 14.3%.

3. Results and Discussions

3.1 Quality of Silage

The result of the determination of usage following the method of Lepper and Flieg (1938), is shown in Table 3.

TABLE 3. — Quality characteristics of the Italian ryegrass silage.

Quantity of ensiled material (kg)	Number of silo's	Treatment (*)	Type and amount of additive	Quality characteristics				
				pH	% acetic acid	% butyric acid	% lactic acid	NH$_3$-N (% of total N
2 600	2	H	aucun-(témoin) no-(control)	3,81	0,60	0,10	1,39	7,8
2 600	2	H	NH$_2$SO$_3$H 0,5 %	3,84	0,44	0,10	1,38	7,8
2 530	2	H	NH$_2$SO$_3$H 1 %	3,44	0,42	0,04	1,40	4,4
2 000	2	N.H.	aucun-(témoin) no-(control)	3,99	0,58	0,38	1,55	8,7
2 000	2	N.H.	NH$_3$SO$_3$H 0,5 %	3,80	0,39	0,35	1,59	5,7
2 000	2	N.H.	NH$_2$SO$_3$H 1 %	3,78	0,35	0,25	0,86	8,9

(*) H = hâché (chopped) ; N.H. = non hâché (no chopped).

As shown in Table 3, all the objectives were mediumly well to well-attained. The pH was always less than 4.2. With one exception, the amidosulphonic acid slightly increased the degree of acidity of all the silage treated.

Conforming to these favorable pHs, the percentage of lactic acid from the different silos reached an elevated level. The percentage of lactic acid did not, on the other hand, rise appreciably following the addition of the preservative; also, it should be noted as well that there was a high percentage of this acid in the control silos. It can be ascertained that the percentage of butyric acid of the chopped fodder (0.08% average) differed substantially from that of the unchopped fodder (0.33% average). In a series of 6 experiments on silage with different kinds of green fodder, of which Italian ryegrass was one, closed clover and a mixture of pea fodder and oats, Buysse (1961), also showed that the chopping favorable influenced the quality of the silage. After experiments on silage with 942 tons of leaves and stems of sugar beets, Boucque and Cottyn (1967) arrived at the same conclusion. The addition of a preservative had the effect of lowering the percentage of acetic acid. The fraction NH which is a direct indication of the decomposition of proteins in the silo, is in all cases less than 10; this value constitutes according to Vaubelle (1958), the maximum value for successful ensilage.

3.2. Balance Sheet for Silage

Table 4 gives a picture of the weight loss in the dry material as well as in the digestible crude protein and the digestible true protein.

TABLE 4. - Losses of the different nutrients (%).

Type and amount of additive	Number of silo's	Treat-ment (*)	Weight losses (%)	% Losses		
				Dry matter	Digest. crude protein	Digest. true protein
aucun-(témoin) no-(control)	2	H	26.1	22.8	6.3	63.0
NH₂SO₃H 0.5 %	2	H	16.5	10.3	+ 25.0	63.8
NH₂SO₃H 1 %	2	H	15.9	2.4	+ 40.9	43.3
aucun-(témoin) no-(control)	2	N.H.	30.5	25.3	12.4	57.1
NH₂SO₃H 0.5 %	2	N.H.	21.6	17.0	+ 6.5	49.9
NH₂SO₃H 1 %	2	N.H.	17.5	17.5	+ 11.6	50.4

(*) H = hâché (chopped) ; N.H. = non hâché (no chopped).

Thus, as it is shown in this table, the favorable effect of the
well
amidosulfonic acid, as/as the weight loss in the dry material, is clear,

and is as evident in the chopped fodder as in that which was ensiled as is.

In relation to the 0.5% concentration, the 1% concentration generally

had the effect of reducing alittle more the losses in both the chopped

and unchopped fodder.

Brown (1960) made a comparison of the losses form silage of prairie

grass preserved in part with 1% amidosulphonic acid and in another part

with molasses. The silage to which was added sulfamic acid or amidosulphonic

acid showed losses of dry material of 16%, while these losses in the silos

treated with molasses amounted to 19%.

In the different experiments done on preservatives, one finds important

favorable results concerning digestible crude proteins. Brown (1960) made

the same statement in his previously cited experiments. These positive results proceed logically from the fact that with the preservative a considerable quantity of N is added to the fodder.

3.3 Ingestion of the Silage by Livestock

As we have already indicated above, the control silage as well as that to which the preservative was added, was fed as the only constituent of their diet to a group of gestating and non-gestating heiffers. The heiffers which received the silage to which was added 1% amidosulphonic acid quickly showed severe diarrhea; two days after putting them back on a diet of the control silage, the consistency of their excrement became normal again. Another feeding of the same experimental silage again caused severe diarrhea. With the silage to which was added 0.5% amidosulphonic acid, nothing abnormal was observed.

With clover ensiled with the equivalent of 12g sulfamic acid (amidosulphonic acid), mixed in the form of dry powder with the fresh material, Martin and Reyntens (1950), also observed severe diarrhea after a few days.

Used in the form of a solution as A.I.V. acid, the product, added in strong concentrations (equivalent to 14g) also caused diarrhea; silage preserved by means of a solution of sulfamic acid (equivalent to 7g) didn't cause any digestive troubles.

Concerning the use of amidosulfonic acid as a preservative, we can conclude by saying that even in a concentration of 0.5%, the addition to ryegrass of an expandable basic powder of this acid favorably influences the weight loss and the losses of dry material.

The feeding of silage to which was added 1% of this preservative always gives rise to serious digestive troubles. These troubles are not

evident when the product is added in a concentration of 0.5% when it is

mixed in a homogenous manner with green fodder at the time of ensilage.

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La valeur de l'acide amido-sulfonique, comme produit de conservation des ensilages (*)

par B.G. COTTYN et F.X. BUYSSE.

Résumé.

Dans une série d'essais d'ensilage avec du ray-grass d'Italie, nous avons étudié la valeur de l'acide amido-sulfonique, employé comme produit de conservation. L'acide amido-sulfonique, la mono-amine de l'acide sulfurique à formule NH_2SO_3H, est un produit cristallin non-volatil et non-hygroscopique à caractère fortement acide. Le produit de conservation ut ajouté en deux concentrations différentes, à savoir à 0,5 et 1 %, aussi bien au fourrage vert haché qu'à celui qui était ensilé tel quel. Pour chacun de ces traitements, nous avons rempli 6 silos expérimentaux cylindriques en béton, chargés en moyenne de 1 300 kg de fourrage haché et de 1 000 kg de fourrage non-haché. Deux de ces silos expérimentaux étaient des silos-témoins sans produit de conservation, deux autres étaient additionnés d'acide amido-sulfonique à raison de 0,5 % et aux 2 derniers ce produit de conservation était ajouté dans une concentration de 1 % (voir schéma expérimental au tableau 1).

Des divers *critères de qualité* (tableau 3) il ressort que tous les objectifs étaient, moyennement bien atteints, le pH était toujours inférieur à 4,2 et était accompagné d'une forte teneur correspondante en acide lactique dans tous les silos.

La teneur en acide butyrique était insignifiante dans l'ensilage haché et atteignait en moyenne un pourcentage de 0,33 % pour les ensilages non hachés. Le produit de conservation avait une influence nettement favorable sur les *pertes en poids* et *les pertes en matière sèche*, aussi bien dans les ensilages hachés que non-hachés (tableau 4).

La teneur en azote relativement élevée du produit de conservation (14,3 %) peut être pour le ruminant une source précieuse de N.

L'affouragement d'ensilage additionné de 1 % d'acide amido-sulfonique, a donné lieu à de sérieux troubles de digestion (diarrhée) chez des génisses. L'ensilage contenant une dose de 0,5 % de ce produit était par contre bien supporté.

1. *Introduction.*

Le groupe de produits de conservation, employé avec le plus de succès lors de l'ensilage de différents fourrages verts non-préfanés, est à base d'acides minéraux forts (Virtanen, 1947). La baisse rapide du pH, provoquée par l'adjonction d'acides forts, guide favorablement le processus de fermentation. Dans le milieu à degré d'acidité élevé ainsi obtenu (pH < 4,2), seules les bactéries d'acide lactique se trouvent dans des conditions favorables de développement, tandis que les bactéries d'acide butyrique et les micro-organismes protéolytiques se voient inhibés dans leur développement. Des acides minéraux forts à l'état liquide, tels que le H_2SO_4, le HCl (acide A.I.V.) et l'acide phosphorique (fossilan) ou des acides organiques moins forts en concentration suffisante, tel que l'acide formique, sont efficaces pour l'obtention d'un pH optimum. Les dangers inhérents à la manipulation de ces liquides fortement corrosifs ont toutefois donné lieu à la mise en vente d'additifs épandables. Il s'agit de poudres dans lesquelles les acides forts sont dispersés, tel le Protosil à base d'acide phosphorique, de mélasse et de tourbe moulue (Cottyn et al., 1969), ou bien d'acides forts sous forme cristalline, ou encore de produits chimiques dont on attend un effet favorable lors de l'ensilage.

L'acide mono-sulfonique, ou le mono-amine de l'acide sulfurique à formule NH_2SO_3H est un produit cristallin non-volatil et non hygroscopique à caractère fortement acide. Les solutions aqueuses ont un degré d'acidité comparable à celui d'une solution de H_2SO_4 ou de HCl de concentration moyenne. C'est ainsi qu'une solution aqueuse de l'acide amido-sulfonique à 1 % a un pH de 1,18. Le produit n'a aucune toxicité spécifique et ne provoque, lors des manipulations, aucun effet irritant permanent digne d'être mentionné.

Dans le but d'étudier la valeur de l'acide amido-sulfonique en tant que produit de conservation, nous avons procédé à une série d'essais d'ensilage avec du ray-grass d'Italie. Le produit était ajouté au fourrage, ensilé à l'état haché ou tel quel, en deux concentrations différentes à raison de 0,5 et de 1 %.

2. Matériel expérimental et techniques employées.

Le fourrage vert provenait d'une première coupe de ray-grass d'Italie. Il fut ensilé dans 12 petits silos expérimentaux cylindriques en béton, pouvant contenir en moyenne 1 300 kg de fourage haché et 1 000 kg de produit non-haché. Pour le hachage, il fut fait appel à une hacheuse stationnaire. Sur les six silos expérimentaux de chaque traitement — matériel haché et non-haché, il y avait chaque fois 2 silos-témoins sans produit de conservation, deux autres additionnés d'acide amido-sulfonique dans une concentration de 0,5 %, et les deux derniers additionnés de 1 % de ce même acide.

Le tableau 1 donne un aperçu schématique de ces expériences.

TABLEAU 1. — Schéma expérimental des ensilages (ray-grass d'Italie).

Quantités ensilées (kg)	Nombre de silos	Traitement (*)	Produit de conservation.	
			Nature	Dose %
2 600	2	H	aucun-(témoin) no-(control)	
2 600	2	H	NH_2SO_3H	0,5 %
2 530	2	H	NH_2SO_3H	1 %
2 000	2	N.H.	aucun-(témoin) no-(control)	
2 000	2	N.H.	NH_2SO_3H	0,5 %
2 000	2	N.H.	NH_2SO_3H	1 %

Ensiled material (kg)	Number of silo's	Treatment (*)	Type	Amount %
			Additive	

(*) H = haché (chopped) ; N.H. = non haché (no chopped).

TABLE 1. — Planned silage experiments (Italian ryegrass).

Après le remplissage des silos, le fourrage était recouvert d'une bâche en plastic et chargé d'une couche de 30 cm de terre. Les silos étaient surmontés de petits toits individuels en zinc afin d'empêcher la pénétration de l'eau de pluie. L'ensemble de la batterie de silos expérimentaux était équipé d'un drain ouvert qui fut fermé après 14 jours.

Au moment de leur sortie du silo, les ensilages étaient affouragés à un groupe de génisses et étaient l'unique constituant de leur ration.

La composition chimique des deux fourrages frais (hachés ou non) et des différents ensilages, obtenus avec ou sans produit de conservation, figure au tableau 2. Au moyen de prélèvements à la main, faits au hasard à différents endroits du matériel frais, on a composé par silo un échantillon moyen. En ce qui concerne le fourrage frais, seule la composition moyenne par traitement (haché et non haché) figure au tableau. Pour le fourrage ensilé, on y trouve l'analyse moyenne par traitement (2 silos).

TABLEAU 2. — Composition chimique du ray-grass d'Italie frais et des ensilages de ce fourrage.

Fourrage grossier	Nature et dose du produit de conservation	Nombre de silos	Traitement (*)	Matière sèche (%)	Composition de la matière sèche (%)			
					Protéines brutes	Protéines brutes digestibles	Protéines réelles	Protéines réelles digestibles
Ray-grass d'Italie (produit frais) Italian ryegrass (fresh material)	—		H	16,38	12,36	8,97	10,98	7,57
Ensilage Silage	aucun-(témoin) no-(control)	2	H	16,28	12,96	10,44	6,33	3,75
	NH₂SO₃H 0,5 %	2	H	17,89	14,98	12,97	5,09	3,02
	NH₂SO₃H 1 %	2	H	19,31	15,33	12,89	6,68	4,25
Ray-grass d'Italie (produit frais) Italian ryegrass (fresh material)	—		N.H.	18,13	11,42	9,19	9,59	7,32
Ensilage Silage	aucun-(témoin) no-(control)	2	N.H.	17,62	14,19	11,01	7,72	4,54
	NH₂SO₃H 0,5 %	2	N.H.	19,50	13,85	11,44	6,51	4,15
	NH₂SO₃H 1 %	2	N.H.	19,42	16,07	13,03	7,21	4,17
Roughage	Type and amount of additive	Number of silo's	Treatment (*)	Dry matter (%)	Composition of the dry matter %			
					Crude protein	Digestible crude protein	True protein	Digestible true protein

(*) H = hâché (chopped) ; N.H. = non hâché (no chopped).

TABLE 2. — Chemical composition of the fresh and ensiled Italian ryegrass.

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Il ressort du tableau 2 qu'après ensilage des fourrages hachés tant que non-hâchés, les teneurs en *protéines brutes* ainsi qu'en *protéines brutes digestibles* dans la matière sèche ont augmenté. Cette augmentation est plus grande dans les silos additionnés du produit de conservation que dans les silos-témoins ; en règle générale, elle est la plus importante dans les silos où le produit de conservation est le plus concentré. Ces augmentations s'expliquent par la teneur en N du produit de conservation.

Par contre, la teneur en *protéines réelles* et en *protéines réelles digestibles* diminue, après ensilage, tant dans le matériel haché que dans celui ensilé tel quel; cette baisse est la plus forte dans les silos expérimentaux additionnés de 0,5 % de produit de conservation.

Il est clair que l'augmentation progressive de la teneur en protéines, au fur et à mesure que la dose de produit de conservation devient plus grande, est essentiellement due à l'adjonction de l'azote contenu dans le produit de conservation. La teneur en N du produit de conservation est en effet de 14,3 %.

3. *Résultats et discussions.*

3.1. *Qualité de l'ensilage.*

Les résultats des déterminations d'usage, d'après la méthode Lepper und Flieg (1938), figurent au tableau 3.

TABLEAU 3. — Qualité de l'ensilage de ray-grass d'Italie.

Matériel ensilé (kg)	Nombre de silos	Traitement (*)	Nature et dose du produit de conservation	Critères de qualité				
				pH	% d'acide acétique	% d'acide butyrique	% d'acide lactique	NH₃-N (en % du N-total)
2 600	2	H	aucun-(témoin) no-(control)	3,81	0,60	0,10	1,39	7,8
2 600	2	H	NH₂SO₃H 0,5 %	3,84	0,44	0,10	1,38	7,8
2 530	2	H	NH₂SO₃H 1 %	3,44	0,42	0,04	1,40	4,4
2 000	2	N.H.	aucun-(témoin) no-(control)	3,99	0,58	0,38	1,55	8,7
2 000	2	N.H.	NH₂SO₃H 0,5 %	3,80	0,39	0,35	1,59	5,7
2 000	2	N.H.	NH₂SO₃H 1 %	3,78	0,35	0,25	0,86	8,9
Quantity of ensiled material (kg)	Number of silo's	Treatment (*)	Type and amount of additive	Quality characteristics				
				pH	% acetic acid	% butyric acid	% lactic acid	NH₃-N (% of total N)

(*) H = hâché (chopped) ; N.H. = non hâché (no chopped).

TABLE 3. — Quality characteristics of the Italian ryegrass silage.

TABLEAU 3. — Qualité de l'ensilage de ray-grass d'Italie.

Matériel ensilé (kg)	Nombre de silos	Traitement (*)	Nature et dose du produit de conservation	Critères de qualité				
				pH	% d'acide acétique	% d'acide butyrique	% d'acide lactique	NH_3-N (en % du N-total)
2 600	2	H	aucun-(témoin) no-(control)	3,81	0,60	0,10	1,39	7,8
2 600	2	H	NH_2SO_3H 0,5 %	3,84	0,44	0,10	1,38	7,8
2 530	2	H	NH_2SO_3H 1 %	3,44	0,42	0,04	1,40	4,4
2 000	2	N.H.	aucun-(témoin) no-(control)	3,99	0,58	0,38	1,55	8,7
2 000	2	N.H.	NH_2SO_3H 0,5 %	3,80	0,39	0,35	1,59	5,7
2 000	2	N.H.	NH_2SO_3H 1 %	3,78	0,35	0,25	0,86	8,9
Quantity of ensiled material (kg)	Number of silo's	Treatment (*)	Type and amount of additive	Quality characteristics				
				pH	% acetic acid	% butyric acid	% lactic acid	NH_3-N (% of total N)

(*) H = hâché (chopped) ; N.H. = non hâché (no chopped).

TABLE 3. — Quality characteristics of the Italian ryegrass silage.

Ainsi qu'il ressort du tableau 3, tous les objectifs étaient *moyennement bien* à *bien* atteints. Le pH était toujours inférieur à 4.2. A une exception près, l'acide amido- sulfonique avait légèrement augmenté le degré d'acidité de tous les ensilages traités.

Conformément à ces pH favorables, les *teneurs en acide lactique* des différents silos atteignaient un niveau élevé. Les teneurs en acide lactique n'avaient, par contre, pas connu de hausse appréciable à la suite de l'adjonction du produit de conservation: à noter d'ailleurs également une forte teneur de cet acide dans les silos-témoins. On a pu constater que la *teneur en acide butyrique* du fourrage haché (de 0.08 % en moyenne) différait sensiblement de celle du fourrage non-haché (de 0,33 % en moyenne). Dans 6 séries d'essais d'ensilage avec différentes variétés de fourrages verts dont le ray-grass d'Italie, le trèfle incarnat et un mélange de pois fourragers + avoine, Buysse (1961) avait, lui aussi, trouvé que le hachage influence favorablement la qualité de l'ensilage. Après des essais d'ensilage avec 942 t. de feuilles et de collets de betteraves sucrières, Boucqué und Cottyn (1967) étaient arrivés à la même conclusion. L'adjonction du produit de conservation a eu pour effet d'abaisser la *teneur en acide acétique. La fraction NH₃*, qui est une indication directe de la décomposition des protéines dans le silo, est pour tous les objets inférieure à 10 ; cette valeur constitue, d'après Vanbelle (1958) la valeur maximum pour un ensilage réussi.

3. 2. *Bilan des ensilages.*

Le tableau 4 donne un aperçu des pertes en poids ainsi que de celles en matière sèche, en protéines brutes digestibles et en protéines réelles digestibles.

TABLEAU 4. — Pertes en différents éléments (%).

Nature et dose du produit de conservation	Nombre de silos	Traitement (*)	Pertes en poids (%)	% de pertes		
				Mat. sèche	Prot. brutes digest.	Prot. réelles digest.
aucun-(témoin) no-(control)	2	H	28,1	22,8	6,3	63,0
NH₂SO₃H 0,5 %	2	H	16,5	10,3	+ 28,0	63,8
NH₂SO₃H 1 %	2	H	15,9	2,4	+ 40,9	43,3
aucun-(témoin) no-(control)	2	N.H.	30,5	25,3	12,4	57,1
NH₂SO₃H 0,5 %	2	N.H.	21,0	17,0	+ 6,5	49,9
NH₂SO₃H 1 %	2	N.H.	17,5	17,5	+ 11,6	50,4
Type and amount of additive	Number of silo's	Treatment (*)	Weight losses (%)	% Losses		
				Dry matter	Digest. crude protein	Digest. true protein

(*) H = haché (chopped) : N.H. = non hâché (no chopped).

TABLE 4. — Losses of the different nutrients (%).

Ainsi qu'il ressort des données de ce tableau, l'influence favorable, exercée par l'acide amido-sulfonique aussi bien sur les *pertes en poids* que sur celles *en matière sèche*, était nette et se manifestait tant dans le fourrage hâché que dans celui qui était ensilé tel quel.

Par rapport à la concentration de 0,5 %, celle de 1 % avait généralement pour effet de réduire encore quelque peu les pertes dans les deux traitements.

Brown (1960) a fait la comparaison des pertes d'ensilages d'herbe de prairie, conservée d'une part avec 1 % d'acide amido-sulfonique et additionnée d'autre part de mélasse. L'ensilage additionné d'acide sulfamique ou d'acide amido-sulfonique présentait des pertes de matière sèche de 16 %, ces pertes étant de 19 % dans les silos traités au moyen de mélasse.

Dans les différents essais réalisés au moyen du produit de conservation, on trouve un important bilan positif, en ce qui concerne *les protéines brutes digestibles.* Brown (1960) fit la même constatation dans les essais précités. Ces bilans positifs résultent logiquement du fait qu'avec le produit de conservation il y a apport d'une quantité considérable de N.

Le bilan des pertes *en protéines réelles digestibles* nous donne de meilleures indications au sujet de la conservation des protéines. Ces pertes, qui dans les silos-témoins atteignent des valeurs très élevées, sont, à une exception près, moindres dans les deux traitements (haché et non-haché) et ce pour les deux concentrations du produit de conservation. Ceci indiquerait, par conséquent, que l'acide sulfamique ou amido-sulfonique serait un stimulant pour une meilleure conservation des protéines de l'herbe. Brown (1960) fait observer, en outre que les apports de N par le produit de conservation peuvent être utilisés efficacement par les bactéries du rumen pour l'élaboration de protéines bactériennes.

3.3. *Ingestion des ensilages par le bétail.*

Ainsi que nous l'avons déjà dit plus haut, aussi bien l'ensilage-témoin que celui additionné du produit de conservation était affouragé en tant qu'élément exclusif de la ration à un groupe de génisses en gestation ou non. Les génisses qui recevaient l'ensilage additionné de 1 % d'acide amido-sulfonique témoignaient assez rapidement d'une forte diarrhée. 2 jours après le remplacement de ce régime par de l'ensilage-témoin, la consistance des excréments était redevenue normale. Un nouvel affouragement du même ensilage expérimental provoquait de nouveau de fortes diarrhées. Avec les ensilages additionnés de 0,5 % d'acide amido-sulfonique, on n'observa rien d'anormal.

Avec du trèfle ensilé avec l'équivalent de 12 g. d'acide sulfamique (acide amido-sulfonique), mélangé sous forme de poudre sèche avec la matière fraîche, Martin et Reyntens (1950) ont également constaté de fortes diarrhées après quelques jours.

Utilisé sous forme de solution comme l'acide A.I.V., le produit, additionné en forte concentration (14 g. eq.), produisait également de la diarrhée; des ensilages, conservés au moyen d'une solution d'acide sulfamique (7 g. eq.), ne provoquaient pas de troubles de la digestion.

En ce qui concerne l'emploi d'acide amido-sulfonique comme produit de conservation, nous pouvons *conclure* en disant que, même dans une concentration de 0,5 %, l'adjonction à du ray-grass d'une poudre épandable à base de cet acide influençait favorablement les pertes en poids et en matière sèche.

L'affouragement d'ensilage additionné de 1 % de ce produit de conservation donnait toutefois lieu à des troubles sérieux de la digestion. Ces troubles ne se manifestaient pas lorsque le produit était ajouté dans une concentration de 0,5 %, à condition qu'il ait été mélangé d'une manière homogène avec le fourrage vert au moment de l'ensilage.

Gontrode, (Kouter, 6) janvier 1969.

SUMMARY.

Amidosulphonic acid as silage additive.

In order to test the value of the silage-additive « amidosulphonic acid » we conducted ensiling experiments with Italian ryegrass. Amidosulphonic acid, the mono-amine of sulphuric acid (NH_2SO_3H) is a non volatile, non hygroscopic cristalline produkt with strong acid characteristics. The additive was used in 2 different concentrations of 0,5 and 1 % to as well chopped as no chopped Italian ryegrass. For each of the treatments we used 6 round concrete silo's. The silo's were filled with 1 300 kg chopped and 1 000 kg of no chopped material (table 1: planned silage experiments). It appears from the different *quality characteristics* (table 3) that the silages were all sucessful.

On all treatments we noted a low pH ($< 4,2$) and a corresponding high lactic acid content. Practically no butyric acid for the chopped but a level of 0,33 % for the no chopped silages was observed. The additive had a favourable influence on as well the weight losses as the losses of dry matter (table 4).

The relative high N content of the conservative (14,3 %) can be a worthful N source for the ruminant. Feeding of silage conserved with 1 % amidosulphonic acid resulted in extreme scouring. We stated no diarrhee on the silages treated with 0,5 % of the additive.

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SULFAMIC ACID . . . . . An Industrial Review

M. E. CUPERY AND W. E. GORDON

E. I. du Pont de Nemours & Company, Inc., Wilmington, Del.

FOR many years sulfamic acid was known as an obscure laboratory chemical which possessed some rather unusual properties of interest only to scientific investigators. Considerable fundamental information concerning its physical and chemical properties was therefore already available when a new and practical process for its manufacture was discovered (14). During the four years which have followed the announcement of this new process, the commercialization of sulfamic acid has rapidly expanded, and today this former curiosity is being produced on a commercial scale and is now available in carload quantities. The purpose of this paper is to review briefly the chemistry of sulfamic acid and its derivatives and to discuss a number of industrial applications for them.

Audrieth and his students (2) published an excellent review of the chemistry of sulfamic acid and related aquo-ammonosulfuric acids. Some of the data which follow were taken from it and from the literature in general. The relationships of sulfamic acid with both the inorganic and organic fields of chemistry are presented in Table I and as follows:

Sulfuric acid   Sulfamic acid   Sulfamide

Imidodisulfonic acid   Imidodisulfonamide   Nitrilosulfonic acid
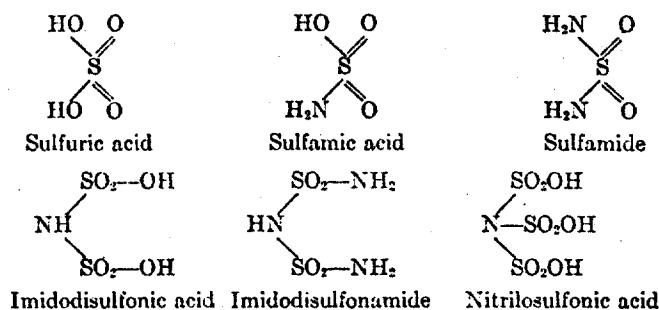
The chemical structure of sulfamic acid as the half amide of sulfuric acid is here brought out. Replacement of both hydroxyl groups of sulfuric acid with amide groups yields sulfamide. Sulfonation of sulfamic acid yields imidodisulfonic acid, and a third sulfonic acid substitution yields nitrilosulfonic acid. Both the imido- and the nitrilosulfonic acids are unstable in the free acid condition and are rapidly hydrolyzed into sulfamic acid which is known to be comparatively stable in aqueous solutions at ordinary temperatures. The salts of these acids, similar to the sulfamates, are comparatively stable in neutral or alkaline solutions. Upon alkaline hydrolysis, sulfamide yields ammonia and the corresponding sulfamate.

TABLE I. MIXED AQUO-AMMONO ACIDS

Related to Sulfuric Acid		Related to Carbonic Acid	
Formula	Name	Formula	Name
HO—SO₂—OH	Sulfuric acid	HO—CO—OH	Carbonic acid
HO—SO₂—NH₂	Sulfamic acid	HO—CO—NH₂	Carbamic acid
H₂N—SO₂—NH₂	Sulfamide	H₂N—CO—NH₂	Carbamide (urea)
HN(SO₂—NH₂)₂	Imidodisulfonamide	HN(CO—NH₂)₂	Biuret
NH(SO₂—OH)₂	Imidodisulfonic acid	HN(CO—OH)₂	Imidodicarbonic acid

Table I illustrates the relation between the nitrogen-substituted sulfuric acid and the nitrogen-substituted carbonic acid series.

While this tabulation illustrates the relationships in structure and composition, the chemical relationships also hold quite well if the greater stability of the sulfuric acid series is taken into consideration. For example, carbamic acid and the carbamates are easily hydrolyzed while sulfamic acid and the sulfamates are comparatively stable.

Physical and Chemical Properties

The more important properties upon which, in most instances, the industrial uses of sulfamic acid are based are as follows: It is a solid melting at 205° C.; it is colorless,
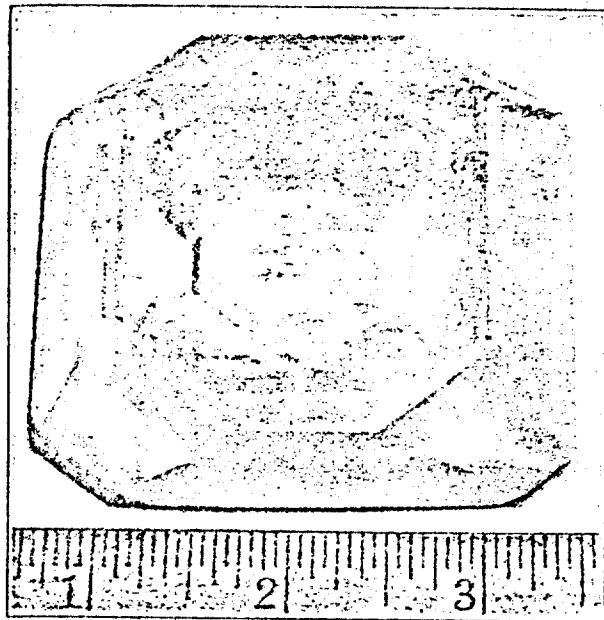
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FIGURE 1. CRYSTAL OF SULFAMIC ACID

single crystal of sulfamic acid shown in Figure 1. This crystal was prepared several years ago by slowly evaporating from a wax-coated container, a saturated solution of sulfamic acid seeded with a single small crystal of the acid. In April, 1938, soon after its preparation, this crystal was exhibited at the meeting of the AMERICAN CHEMICAL SOCIETY at Dallas (14). Since that time it has been stored under ordinary room conditions wrapped in cheesecloth. Except for slight loss in luster, this crystal has retained its original appearance. The crystal structure of sulfamic acid has been fairly well defined in several publications (9, 21, 31, 46). In a more recent publication concerning crystal structure of potassium sulfamate it is concluded that the three oxygens and the nitrogen atom of the sulfamate group are arranged in an almost regular tetrahedron configuration around the sulfur atom. The structure appears to be purely ionic, and there was no evidence of hydrogen bridges between neighboring anions (7).

The chemical properties of sulfamic acid were discussed in considerable detail in a previous publication (14), and the more important of these properties which are of interest commercially are listed above. It is evident that the chemical character of sulfamic acid depends on both its acidity and on the reactivity of the amide group. These properties will be referred to again in connection with various industrial applications for the acid and its derivatives.

Very little information relating to the physiological properties of sulfamic acid has been published (36, 40). In a preliminary study made by the Haskell Laboratory of Industrial Toxicology, it was found that rather large oral doses of sulfamic acid to rats showed toxicity effects such as might be expected from feeding any highly ionized acid material (25). Moderate doses of either sulfamic acid or ammonium sulfamate (1 gram daily for 6 days) fed to dogs gave no systemic toxic effects. In the latter experiments the sulfamate group was apparently not decomposed in the organism but was excreted unchanged in the urine. Upon brief contact with the skin sulfamic acid shows no noticeable effect but, as a normal safety precaution, it is recommended that prolonged exposures be avoided. Ammonium sulfamate showed no skin irritation on rats. Similarly, in two hundred human test cases supervised by the Haskell Laboratory of Industrial Toxicology, fabric treated with ammonium sulfamate produced no skin irritation.

odorless, nonvolatile, nonhygroscopic, soluble in water and in formamide, and slightly soluble in methanol. Sulfamic acid is highly ionized in aqueous solution, and its pH range approaches that of nitric, sulfuric, and hydrochloric acids (14). It forms highly soluble salts with (a) basic hydroxides —e. g., lead and barium sulfamate—and with (b) amines and polymeric amines. Sulfamic acid contains a reactive amide group, is hydrolyzed by hot water and alcohols, and reacts with nitrous acid and nitric acid, with aldehydes, and with certain amide groups.

It should be emphasized that sulfamic acid shows a unique and important combination of properties in that it is a solid, nonhygroscopic material which is easily packaged and transported commercially, and is also a strong acid which is highly ionized in aqueous solution.

An effective demonstration of the nonhygroscopic, nonvolatile nature of sulfamic acid is afforded by the large

The discovery of a practical process for the manufacture of sulfamic acid has stimulated the development of various industrial uses for this acid and its derivatives. Expansion of these industrial applications now permits the production of sulfamic acid and certain of its salts on a commercial basis. The physical and chemical properties of sulfamic acid upon which these industrial uses are based are reviewed, and information obtained in a preliminary study of the physiological properties of sulfamic acid and ammonium sulfamate is given.

Among the more important practical applications reviewed in some detail are the following: nitrite removal in diazotization reactions, analytical procedures, laboratory reagent, flameproofing textiles, leather tanning, weed killing, aldehyde-addition reactions, and electroplating. Among the miscellaneous potential applications for sulfamic acid recently disclosed in the patent literature are: laundry sours, gas-liberating compositions, metal polishes, photographic compositions, solubilizing polymeric or high-molecular-weight amines, peptizing pigments, polymerizing olefins, and acidizing oil wells. Sulfamic acid can now be considered as an available raw material destined to become of increasing industrial importance.

Reaction with Nitrous Acid

One of the first industrial applications to be developed for sulfamic acid was based on its reaction with nitrous acid (23). The chemistry of this application is represented by the following equation:

$$HO-SO_2-NH_2 + HNO_2 \longrightarrow H_2O + N_2 + H_2SO_4$$
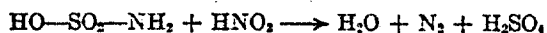
This reaction is exceedingly rapid and proceeds quantitatively, as shown a number of years ago by Baumgarten and Marggraff, who recommended the use of sulfamic acid in an improved analytical procedure for the determination of nitrites (4). Recently this treatment for nitrite removal has been utilized in analytical procedures for determining dissolved oxygen and biochemical oxygen demand in sewage treatment and river pollution studies (13). A similar procedure for nitrite removal has been proposed in a method for analyzing the sulfanilamide content of blood (41). These investigations further substantiate the quantitative nature of this reaction. Of more direct commercial interest is the use of sulfamic acid for eliminating the excess nitrite employed in diazotization reactions for dye and colored pigment manufacture (37). In a representative pigment manufacturing process which originally required 25 pounds of urea and a period of 3 hours to complete the excess nitrite removal, 4 pounds of sulfamic acid now complete the same reaction in about 5 minutes. Similar results are obtained in azo dye manufacture. In such procedures a larger excess of nitrite may frequently be employed to facilitate the diazotization. Because the reaction may be more closely controlled, cleaner shades of color with better uniformity in batches is possible. The advantages of these procedures are now being extended to other fields such as in the application of developed colors to textiles and leather.

Flameproofing

An early observation that the sulfamates are highly compatible with cellulose led to their extensive evaluation as flameproofing agents (15, 16). Ammonium sulfamate is unique among ordinary fire retardants because it does not cause stiffening or otherwise adversely affect the handle and feel of fabrics, paper, and the like. Moreover, the sulfamates show no tendency to crystallize on the surface of the flameproofed article on aging (15). Wearing apparel treated with ammonium sulfamate retains its original appearance and texture and in practical uses, such as workmen's overalls, has shown no decrease in wearing quality. Flameproofed draperies which are often exposed to wide variations in temperature and humidity show no efflorescence of the sulfamate upon the surface of the fabric. Under certain special conditions where a slight afterglow cannot be tolerated or where exceptionally high humidities are encountered, modified compositions of ammonium sulfamate are recommended (22). The applications are made from aqueous solutions by either dipping or spraying methods. The treatment is resistant to dry cleaning solvents but is rapidly removed by water. Considerable amounts of ammonium sulfamate fire retardant were used at both the San Francisco and the New York World Fairs. Appreciable quantities of this fire retardant are now being utilized in airplane manufacture and in flameproofing workmen's clothing for greater protection—for example, in steel mills, shipbuilding plants, and welding operations. Because of numerous fires, particularly those in entertainment halls, many cities throughout the country now enforce strict ordinances requiring a fire retardant treatment for all decorative materials, draperies, window curtains, etc., used in places of public assembly. The demand for a satisfactory fire retardant has increased substantially during the last few years.

Laboratory Reagent

Another general application for sulfamic acid is as a laboratory reagent in both industrial and institutional laboratories. A number of such possible uses follow: titrimetric standard (indicator pH range 4.5-9); diazotization reactions (dye preparations); analytical procedures for nitrite analysis and oxygen in water analysis; extraction of rare earth metals; miscellaneous experimental uses, such as preparing nitrous oxide from nitric acid and sulfamic acid, and determining water of hydration in calcium sulfamate.

Investigations by Audrieth and his students showed that sulfamic acid is an excellent acidimetric reference standard in analytical chemistry, and is superior to such standards as benzoic acid, succinic acid, potassium biiodate, and potassium acid phthalate (10). The use of sulfamic acid for reaction with nitrite was described previously, but it might be mentioned that a number of schools have adopted sulfamic acid as a standard reagent in laboratory experiments involving diazotization reactions. The analytical procedures listed above have shown definite advantages and are recommended as standard methods of analysis (4, 13, 41). It is reported that the separation of the lanthanum earth metals from the yttrium rare earth group is facilitated through the use of sulfamic acid (33). In a recent publication King and Hooper showed that hydrated calcium sulfamate is readily dehydrated at temperatures above 69.4 °C. (32). As the hydrated salt is easily prepared in the laboratory, it should be especially suitable for determinations of water of hydration as carried out in elementary chemistry courses. The preparation of nitrous oxide gas is easily accomplished simply by heating nitric acid with sulfamic acid (3). An experiment of this type might well supplement the ordinary laboratory experiment based on a heat decomposition of ammonium nitrate. Additional elementary experiments might be devised in which the solid, nonhygroscopic nature of sulfamic acid would be advantageous because of greater accuracy, convenience, and safety in handling.

Tanning

An extensive evaluation program relating to the use of sulfamic acid in the leather tanning industry has been carried out, and certain advantages have been observed (19). For example, skins processed with sulfamic acid have a finer and silkier grain than those prepared with sulfuric acid. Moreover, sulfamic acid gives a tighter skin and produces better suède when used on goatskin tanned with formaldehyde. The calcium sulfamate formed in the processing is highly soluble so that there is less tendency toward lime spots than when sulfuric acid is used.

In the leather pickling operation in which hides are converted from an alkaline to an acid condition for prolonged preservation, a portion or all of the sulfuric acid may be replaced with sulfamic acid, depending upon the results desired. Higher proportions of sulfamic acid yield leather showing a more attractive grain and better working qualities.

In the regular bating procedure the hides are subjected to the action of enzymes to remove hair follicles and extraneous matter. In this operation approximately 0.25 per cent of sulfamic acid, based on the flesh weight of hides, and the regular amount of bating material or similar products are added to the skins placed in the bating paddle. The temperature should be allowed to rise to the normal point in the tannery, which may vary between 90° and 95° F. If the bating material does not contain ammonium salts, it is desirable to add a small amount of ammonium chloride or sulfate to the bate to prevent surface hardness. The leather produced with sulfamic acid according to the above procedure shows a fine and silky grain which is retained throughout the subsequent finishing operation.

Herbicidal Action

About five years ago the evaluation of sulfamic acid and its salts as weed killers was first initiated. Preliminary reports of this work, published about two years ago (18), stimulated a large number of practical field tests by agents scattered throughout this country and abroad. Highly favorable results are indicated in the reports of practically all of these investigations, from which the following conclusions have now been drawn (20):

1. Ammonium sulfamate has a much more effective herbicidal action than ammonium sulfate, ammonium thiocyanate, sodium chloride, and calcium chloride, and is equally as effective as, or on some weeds is better than, sodium chlorate.

2. Ammonium sulfamate is considerably more effective in herbicidal action, on an equal weight basis, than sodium, magnesium, and calcium sulfamates and is slightly more efficient than sulfamic acid.

3. Certain woody plants such as poison ivy and wild cherry are readily eradicated by proper treatment with ammonium sulfamate spray, used in a concentration of about one pound of salt per gallon of water.

4. Most of the annual weeds and "soft" perennials are easily killed by proper spraying with ammonium sulfamate solution.

5. Certain perennials such as woodbine, bindweed, blackberry, and grasses are somewhat more resistant and may require additional treatment to obtain permanent eradication.

6. Treatments are the most effective when applied to the mature plant during the summer and fall.

7. Conditions of high humidity accelerate the weed-killing action of ammonium sulfamate.

8. The herbicidal action of ammonium sulfamate is probably associated with translocation of the salt into the plant structure, especially through the leaf tissues.

In addition to its outstanding herbicidal action, ammonium sulfamate has several other advantages. It is apparently quite rapidly decomposed by bacteria in the soil (36) so that it may be applied without danger of long-time soil sterilization. In the physiological tests mentioned above, ammonium sulfamate was found to be nontoxic to animals. It does not possess the fire hazard associated with certain weed killers. Ammonium sulfamate may therefore be used advantageously in places where plants are subsequently grown, where toxic materials would be objectionable, or where fire hazards should be avoided.

When ammonium sulfamate solution is applied to a single selected leaf at the top of a growing coleus plant, the treated leaf soon wilts and gradually dies. However, before the treated leaf has completely wilted, other leaves of the plant progressively wilt as ammonium sulfamate is translocated within the plant. If sufficient salt is applied, the entire plant will gradually die (24). When applied only to the bark of the poison ivy vine or of various trees, ammonium sulfamate solution is without effect. Thus it has been found especially suitable for the eradication of poison ivy from orchards; practical tests carried out in Ohio, California, New York, Delaware, and other states, have been highly succesful and have increased the demand for ammonium sulfamate in this field. A considerable number of inquiries have already been received relating to the eradication of poison ivy from parks and recreational camps. In many localities wild cherry is especially obnoxious because it serves as the host for orchard diseases and insect pests. Cutting wild cherry brush is ineffective as a means of eradication, while digging out the roots is expensive and often difficult. Ammonium sulfamate spray is easily applied and serves as an effective control because the entire plant, including the root system, is destroyed. Deeprooted weeds such as Canada thistle and bindweed or certain grasses, notably ordinary quack grass, show complete top kill and considerable root injury, but repeated treatment is often required before permanent eradication is obtained. A somewhat selective weed-killing action has been noted in a few instances, but considerable work remains to be done along this particlar line before definite recommendations are possible (24).

A representative field test showing effective eradication of poison ivy by means of ammonium sulfamate is shown by Figure 2. Each of three test plots had an area of 100 square feet, and a fence post covered with ivy was located at approximately the center of each plot. On June 15, 1940, the foliage was treated with a solution comprising one pound of salt in one gallon of water applied with a pressure sprayer. Ammonium sulfamate was applied to the center post area, ammonium thiocyanate to the plot in the left foreground, and ammonium sulfate to the area surrounding the right-hand post. The photograph was taken on August 10, 1941, 14 months after treatment. Ammonium thiocyanate and ammonium sulfate gave only slight temporary injury during the first season (1940) while ammonium sulfamate gave complete kill. Only annual weeds, presumably started from seeds, were present during the second season (1941) in the ammonium sulfamate treated area.

A discussion of the chemistry of the action of ammonium sulfamate as a herbicide would be highly speculative. It is possible that the slight acidity and high solubility of ammonium sulfamate combined with its compatability with cellulose may be important factors, but there is no evidence to prove this.

FIGURE 2. EFFECTIVE ERADICATION OF POISON IVY WITH AMMONIUM SULFAMATE IN A FIELD TEST

Miscellaneous Uses

An interesting group of compounds derived from the sulfamates are the aldehyde addition products; their structure is represented by the general formula R—CHOH—NHSO$_3$M, or the dehydrated form R—CH=NSO$_3$M, where R designates hydrogen or an organic group and M represents a cation metal or group. Previous publications have described a number of these derivatives and their method of preparation (27, 34, 48, 49). The aldehyde derivatives of calcium sulfamate are of particular interest because of their greater stability, especially in the isolated, solid form (23). Depending on the conditions of preparation, either the calcium methylol sulfamate, (HOCH$_2$NHSO$_3$)$_2$Ca, or the calcium methylene sulfamate, (CH$_2$=NSO$_3$)$_2$Ca, may be prepared. As would be expected, the methylol derivative is highly soluble in water while the methylene derivative is only moderately soluble. Other aldehyde-addition products, such as calcium benzaldehyde sulfamate and calcium furfural sulfamate, are readily prepared using essentially the method described by Schroeter (48). A number of specific uses for these products are now being considered.

Recent publications have indicated that sulfamic acid performs satisfactorily under certain conditions when used for electroplating metals or for refining metals by electrochemical procedures. Metals such as copper, silver, iron, nickel, cobalt, cadmium, zinc, and lead have been satisfactorily plated in smooth deposits from sulfamic acid solutions (11, 12, 42, 44). Certain advantages over fluosilicic acid have also been noted in the refining of lead. For example, sulfamic acid is more easily handled commercially and its solutions may be used in ceramic- or asphalt-coated wood containers. However, further practical testing is required before sulfamic acid will be extensively used in this field (43).

A considerable number of miscellaneous applications for sulfamic acid and its salts have been disclosed in the recent patent literature. Certain of these uses show promise of becoming commercially important although further expansion in the fields indicated will depend mainly on economic considerations balanced against the technical advantages derived through the use of sulfamic acid. Among the applications of sulfamic acid itself are: laundry sour (26), washing rinse or fixing agent for textile dyes, gas liberating compositions (6, 45), metal polishing compositions (5, 29), photographic fixing baths (3), photographic bleaching baths (39), solubilizing high-molecular-weight amines (basic dyes) (47, 52), solubilizing polymeric amines (17), peptizing pigments (35), polymerizing olefins (50), and acidizing oil wells (1, 5). The sulfamates may be utilized as antigelation agents for soap solutions (30), in preparing phthalocyanine pigments (53), in preparing guanidine sulfamate (23), and as textile finishing agents (38, 51).

In each of these applications one or more of the advantageous properties of sulfamic acid or its salts is utilized. For example, when sulfamic acid is used as a laundry sour at the end of a laundry washing operation, less residual inorganic salts remain in the fabric. In small-package textile dye preparations, which may be purchased for home applications, a solid acid ingredient is often included for fixing the dye at the end of the dyeing process. For such usage the acid must be crystalline and nonhygroscopic and, preferably, show high ionization in water. Sulfamic acid meets these requirements. Certain gas-liberating compositions have the advantage that they are comparatively stable in the dry solid form but readily react when water is added. In some instances metal polishing compositions have shown improved scouring and polishing properties when sulfamic acid is used as the acid ingredient. The additional uses listed show advantages mainly based on the ease of handling this acid

commercially and its ability to form strongly acid solutions or highly soluble salts.

Ammonium sulfamate is known to decrease the gelation tendency of soap solutions. This antigelation effect of the sulfamate ion has been noted in other colloidal systems and may well find specific industrial applications.

In summarizing the present commercial position of sulfamic acid, it may be stated that a number of established industrial applications have already been made which permit the manufacture of sulfamic acid on a major scale. Additional practical applications will no doubt be found. Sulfamic acid can now be considered an available, commercial chemical destined to become of increasing industrial importance.

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Dry Acid *dairy cleaners*

based on Du Pont Sulfamic Acid

offer safety, reduced handling

and economy . . .

Ideal
for cleaning

PLATE PASTEURIZERS • PASTEURIZING VATS
HOMOGENIZERS • MILK TANKS
PROCESS LINES

SIX good reasons why
Dry Du Pont Sulfamic Acid
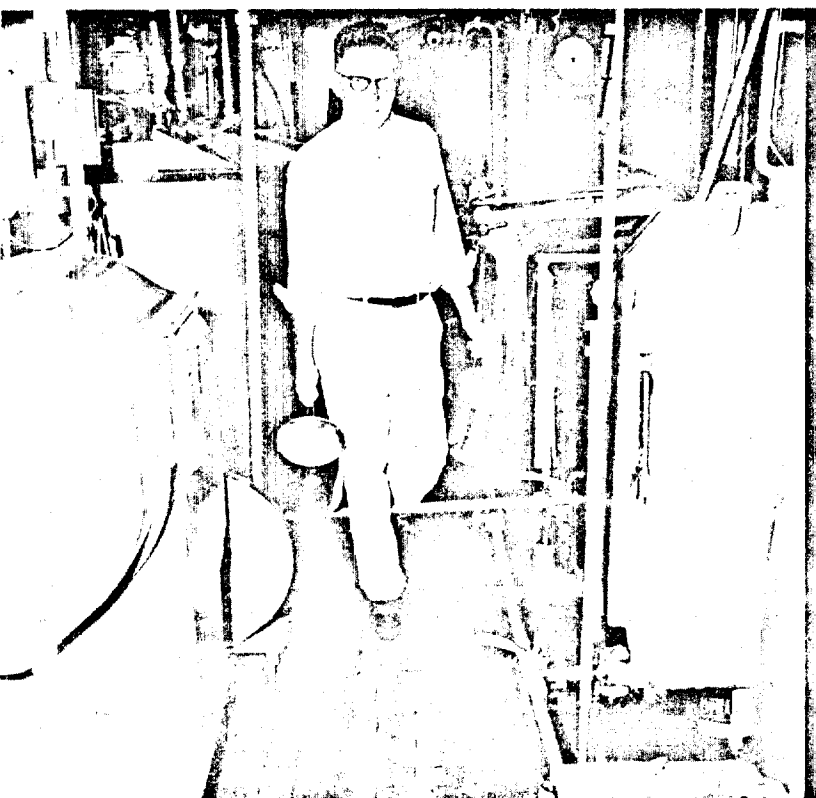
Safer to Handle. There's much less danger in handling sulfamic acid-based cleaners. They are non-irritating to dry skin and can easily be rinsed away with water. Switching to sulfamic-based cleaners means no more hazardous glass bottles to carry over wet, slippery floors; no danger of spilled liquid acid.

Less Expensive to Use. Dry acid cleaners based on sulfamic are usually at least 95% active. That means there are no idle, useless ingredients: practically all of the dry acid cleaner actively works to remove milkstone from process equipment.
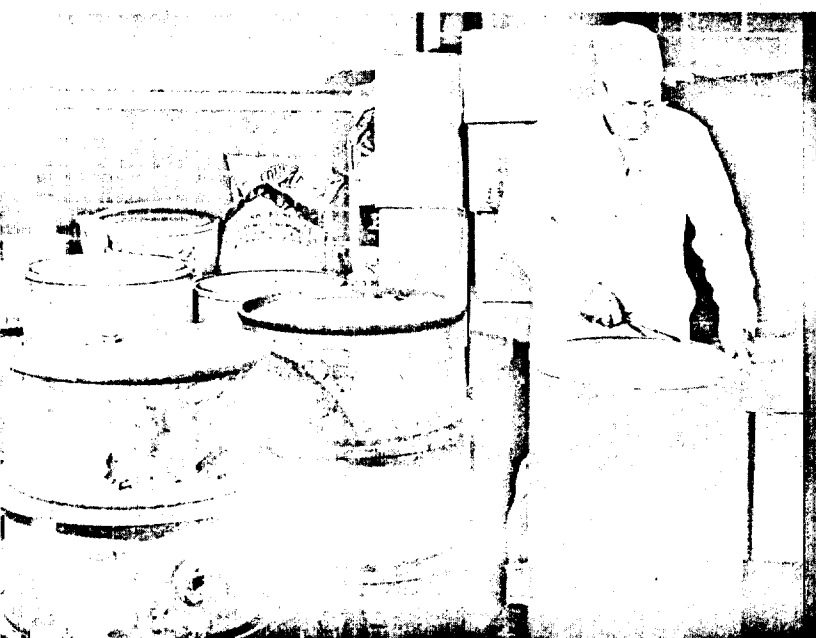
Less Weight to Handle. One 400-lb. drum will replace two 55-gal. drums of 50% liquid acid cleaner that weigh more than 650 pounds each. Thus shipping sulfamic-based cleaners costs less and less space is needed for storage.
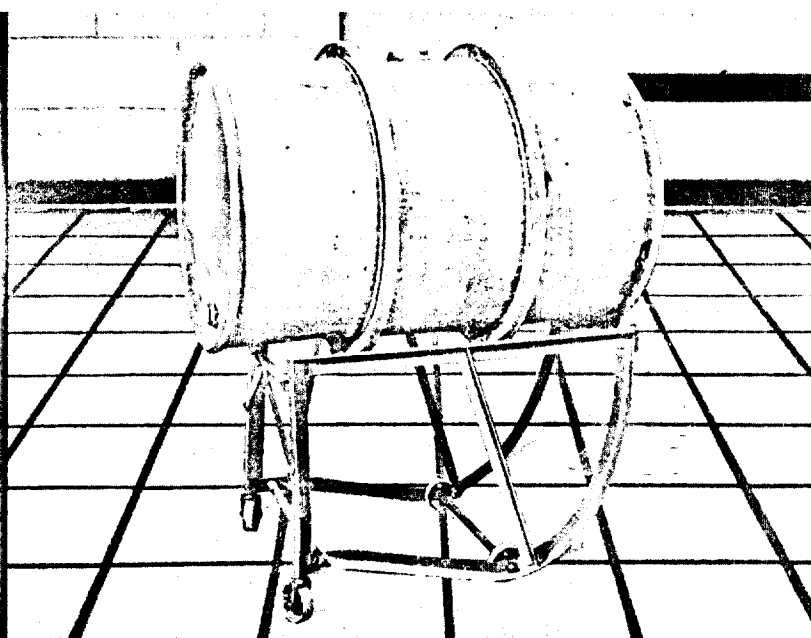
Eliminates Leakers. Even lined steel drums for liquid acids can leak, wasting money and presenting a danger to personnel and equipment. Leakage can cause expensive floor damage.

new cleaners based on
a e ideal for dairy cleaning

Unit Packaging Cuts Waste. At convenient slack times, crystalline dry acid cleaners formulated with Du Pont sulfamic can be weighed out in the exact amount required for each cleaning operation. This unit packaging eliminates over-use by maintenance workers and is conveniently simple and safe.

Quick and Easy to Use. Dry acid cleaners are quickly and easily added directly to surge tanks, vats, etc. Here they rapidly dissolve in water and effectively remove milkstone from process equipment. Special precautions aren't necessary, and personnel need not be experienced in acid handling.

NOW ... YOU CAN CLEAN DAIRY EQUIPMENT MORE SAFELY AND MORE EFFICIENTLY WITH QUICK-ACTING, ECONOMICAL *DRY ACID* CLEANERS

Dry acid cleaning compounds based on Du Pont sulfamic acid are measured dry, then mixed with water for use. These cleaners are non-fuming and produce no corrosive gases, whether dry or in solution. They have been accepted by industry for cleaning equipment ranging from water distilling units, to sugar evaporators. And they can be handled safely by inexperienced workers.

Milk burn-on and milkstone are quickly and thoroughly removed from stainless steel surfaces of process lines, storage tanks and equipment with solutions of these cleaners. Lab tests, confirmed by extensive plant experience, show sulfamic-based cleaners are as gentle as liquid acid cleaners on stainless steel dairy equipment.

Dry acid cleaners are ideal for in-place cleaning of standard equipment used in fluid milk, milk products and ice cream plants. Join the growing number of companies who are saving time and money with cleaning compounds based on dry sulfamic acid!

Get full information today about cost- and time-saving *Dry Acid* Cleaners!

Ask your formulator or dairy supply dealer about these cleaners based on Du Pont Sulfamic Acid. He will gladly discuss your specific cleaning needs, and show you how you can save money and time with these convenient cleaning compounds.

Du Pont manufactures sulfamic acid—does not formulate or sell any cleaning compound based on this chemical. For best results, follow recommendations of the manufacturer whose product you use.

Industrial and Biochemicals Department
E. I. du Pont de Nemours & Co. (Inc.)
Wilmington 98, Delaware

DU PONT
REG. U. S. PAT. OFF.

SULFAMIC ACID

$$H_2N-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$$

Sulfamic acid is a nonvolatile, nonhygroscopic, odorless, white crystalline solid. It forms highly ionized, strongly acidic aqueous solutions. Du Pont manufactures sulfamic acid in both crystalline and granular forms.

AVERAGE ANALYSIS

	CRYSTAL GRADE	GRANULAR GRADE
Sulfamic acid, wt%	99.6	92.3*
U.S.S. Screen Size		
On #16, wt%	0.1-0.6	—
Through #100, wt%	—	4.0

*Remaining 7.7% is primarily ammonium bisulfate.

PROPERTIES

Melting Point, °C	205
°F	401
Solubility in water, wt%	
25°C (77°F)	24
70°C (158°F)	43
pH of a 1% solution	
20°C (68°F)	1.25

CHEMICAL REACTIONS

Reaction with carbonates

$CaCO_3 + 2HSO_3NH_2 \rightarrow Ca(SO_3NH_2)_2 + H_2O + CO_2$

Reaction with basic hydroxides

$KOH + HSO_3NH_2 \rightarrow KSO_3NH_2 + H_2O$
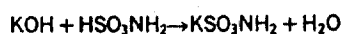
Reaction with metallic oxides

$Fe_2O_3 + 6 HSO_3NH_2 \rightarrow 2Fe(SO_3NH_2)_3 + 3H_2O$

Reaction with nitrous acid

$HNO_2 + HSO_3NH_2 \rightarrow H_2SO_4 + H_2O + N_2$
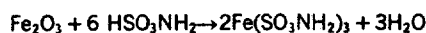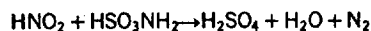
Reaction with sodium hypochlorite

$NaOCl + HSO_3NH_2 \rightleftarrows NaSO_3NHCl + H_2O$

$NaOCl + NaSO_3NHCl \rightleftarrows NaSO_3NCl_2 + NaOH$
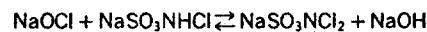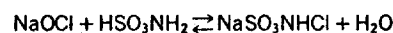
Reaction with tertiary amines

$R_3N + HSO_3NH_2 \rightarrow R_3N \cdot HSO_3NH_2$
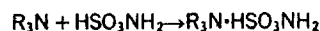
Reaction with primary alcohols

$ROH + HSO_3NH_2 \rightarrow RO-SO_2-ONH_4$

Hydrolysis

$H_2O + HSO_3NH_2 \underset{\Delta}{\rightleftharpoons} NH_4HSO_4$
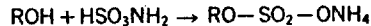
Aqueous solutions hydrolyze very little at room temperature

SUGGESTED USES AND APPLICATIONS

Industrial Cleaning—Because of handling ease and lower corrosiveness the dry acid replaces mineral acids as the active ingredient in chemical cleaners. It is useful for descaling air conditioning, marine, and dairy equipment as well as industrial boilers, condensers, and heat exchangers. It is also used to clean sugar evaporators and as a conditioner to clean paper makers felts, Fourdrinier wires and cylinder molds.

Chlorine Stabilization—By forming chlorosulfamates* with chlorine in water, sulfamic acid acts to stabilize the chlorine used in swimming pools, cooling towers, and paper mills to control microorganisms.

Paper Pulp Bleaching—Sulfamic acid combines with hypochlorites to form chlorosulfamates* which reduce pulp degradation and increase bleaching efficiency.

Dyes and Pigments—Sulfamic acid reacts with nitrous acid to form nitrogen gas. This reaction is used commercially to remove excess nitrate in manufacture of

*Refer to the Du Pont Sulfamic Acid Product Information Bulletin for information on potential hazards from preparation and use of N-chlorosulfamates.

dyes and pigments, and fabric and leather dyeing.

Electroplating and Electroforming—Plating baths of sulfamate metal salts give bright, dense deposits in electroplating and electroforming. Nickel sulfamate baths show increased throwing power and stress-free coatings.

FDA Status—Sulfamic acid may be used in paper and paperboard in contact with food and food products in accordance with applicable FDA regulations. It is authorized for use as an acid cleaner in equipment used in all departments in plants operating under USDA Poultry, Meat, Rabbit, and Egg Products Inspection Programs.

STORAGE AND HANDLING

Sulfamic acid granular should be stored in a cool place. The crystal grade does not require special storage. To prevent the absorption of moisture and possible caking of both granular and crystal grades, package liners should be kept tightly sealed when not in use.

Since aqueous sulfamic acid solutions attack ferrous metals, corrosion-resistant equipment is recommended. Satisfactory materials for storage tanks are polyethylene, rubber lined steel, and type 316 stainless steel with stress relieved welds.

PERSONAL SAFETY

Sulfamic acid and its solutions cause eye injury. Do not get in eyes. Cup-type, rubber, or soft plastic framed goggles, equipped with approved impact-resistant glass or plastic lenses, should be worn. Goggles should be carefully fitted to insure maximum protection and comfort.

In case of contact, flush the eyes with plenty of water for 15 minutes and get medical attention.

Sulfamic acid and its solutions may also irritate the nose, throat, and skin. Avoid breathing dust. Avoid contact with skin and clothing. Exposure to the skin can be minimized by wearing rubber gloves when handling sulfamic acid and its solutions. In case of contact, flush the skin with plenty of water.

For ingestion of sulfamic acid, the person should drink large amounts of water immediately and get medical attention. Vomiting should not be induced.

PACKAGES

Granular—400 lb nonreturnable polyethylene lined fiber drums.

Crystal—50 lb moisture proof polyethylene lined paper bags and 425 lb nonreturnable polyethylene lined fiber drums.

No DOT label is required. Freight classification: Acid Sulfamic, Dry (Acid N.O.I.B.N., Dry).

INDUSTRIAL CHEMICALS
INDUSTRIAL AND BIOCHEMICALS DEPT.

AMMONIUM SULFAMATE

$NH_4SO_3NH_2$

DESCRIPTION

White, odorless, crystalline salt.

TYPICAL ANALYSIS

Ammonium Sulfamate.........................98.9%
Free Sulfate as $(NH_4)_2 SO_4$......................1.1%
Iron as Fe....................................0.001%
Water Insoluble Matter......................0.006%
Moisture 0.02%

pH of AMMONIUM SULFAMATE SOLUTIONS

DATA	
%	pH
10	5.12
6	5.18
5	5.20
2.5	5.29
1	5.40
.5	5.60
.25	5.74
.10	6.00
.05	6.21
.01	6.42

Concentration
% by wt.
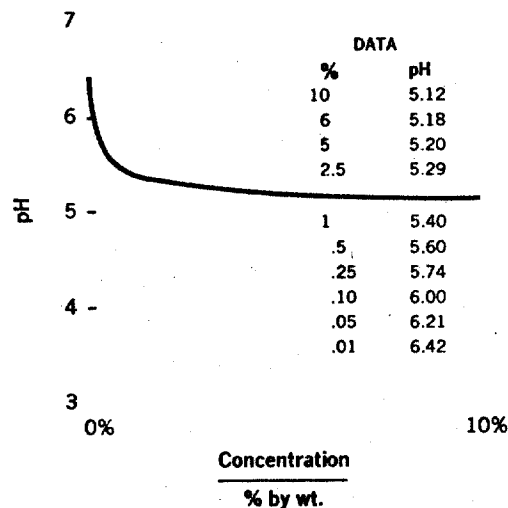
PHYSICAL PROPERTIES

Molecular Weigh 114.13
Melting Point...........................131 to 132°C
Bulk Density (59-lbs/cu ft loose, 65 packed)

CHEMICAL REACTIONS

Ammonium sulfamate reacts with:

1—Benzamide, to yield diammonium imidodisulfonate,
$C_6H_5CONH_2 + 2NH_4SO_3NH_2 + H_2O \rightarrow$
$HN (SO_3NH_4)_2 + C_6H_5COOH + 2NH_3$
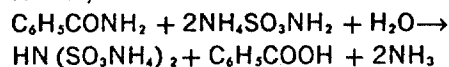
2—Urea, to yield guanidine sulfate,
$H_2N \cdot C:ONH_2 + NH_4SO_3NH_2 \rightarrow$
$H_2N \cdot C:NHNH_2 \cdot NH_4HSO_4$
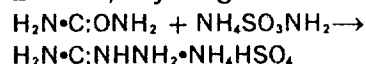
3—Urea, at elevated (250°-400°C) temperatures, to yield melamine,
$3H_2N \cdot C:ONH_2 + 3NH_4SO_3NH_2 \rightarrow$
$(H_2NCN)_3 + 3 (NH_4)_2 SO_4$
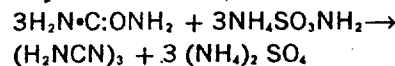
4—Amides, by fusion, to yield nitriles; typically,
$RCONH_2 + NH_4SO_3NH_2 \rightarrow RCN + NH_4HSO_4 + NH_3$

5—Water, at elevated temperatures (80°C and up), hydrolyzing to form ammonium sulfate. (See section on "Safe Handling")—
$H_2O + NH_4SO_3NH_2 \rightarrow (NH_4)_2 SO_4 + heat$
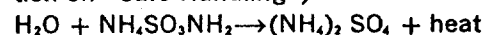
6—Aldehydes, at low temperatures (10°C and down),
$CH_3CHO + 2NH_4SO_3NH_2 \rightarrow$
$NH_4SO_3NHCHOHCH_3 + (NH_4)_2 SO_4$
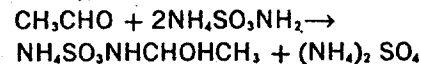
DENSITY OF AQUEOUS SOLUTIONS

Concentration % by Wt of Ammonium Sulfamate in Water	Specific Gravity at 25°C
0%	0.9971
5%	1.0221
10%	1.0468
15%	1.0717
20%	1.0964

SOLUBILITY IN WATER

g/100g H_2O	Temp.
134.8	0.2
166.6	10
200.2	20
234.4	30
279.5	40
357	50

DATA

gms. Ammonium Sulfamate
───────────────────────
100 grams H_2O
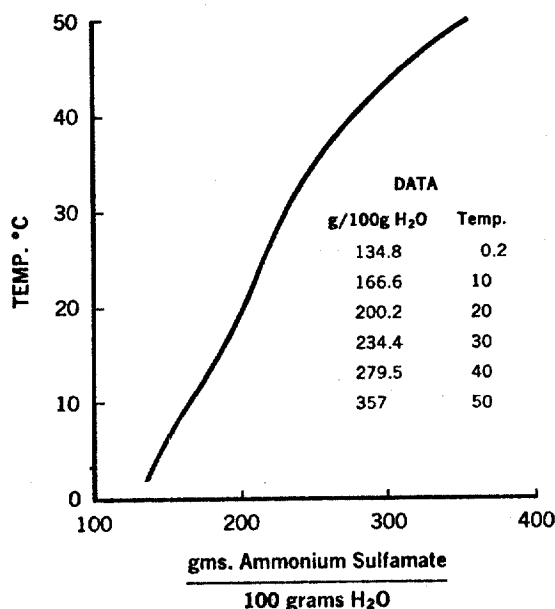
Moderately soluble in glycerine, glycol,
formamide and liquid ammonia.

USES

ANTI-GELLANT Ammonium sulfamate shows less tendency to coagulate many colloids than salts of other acids. Addition of 10% ammonium sulfamate in soap or sulfonated detergent solutions often prevents gelling, even at room temperatures, thus avoiding the need to keep these solutions hot.

TEXTILE FINISHING Ammonium sulfamate imparts a soft "hand" to cotton textiles at loadings of 8-12%.

FLAME RETARDANT FOR FABRICS Approved by the Board of Standards and Appeals of the City of New York, January 14, 1941, under Cal. No. 822-40-SM. Recommended only for cellulosic fabrics.

FLAME RETARDANT COMPOSITIONS Combined with other materials for use as a flame retardant for paper and fabrics. A typical formula is one recommended in the American Hotel Association's report, "Textile Flame-proofing Compounds, Part I", which lists "80 lbs of ammonium sulfamate, 20 lbs diammonium phosphate, ¾ oz. Nacconol NRSF* (wetting agent), and 50 gallons of water". In any such flame retardant formula it is essential to test swatches of each batch treated for flame retardancy. A weighting of 15% dry solids based on the dry weight of fabric treated is suggested.

*Allied Chemical Co., National Aniline Div.

FLAME RETARDANT—WATER REPELLENT COMPOSITIONS Du Pont has in its research laboratories in recent years invented an improved flame retardant and water repellent composition highly useful in the treatment of organic materials. This composition contains four essential ingredients as follows:—

Ammonium sulfamate	100 parts by weight
Dicyandiamide*	5-20 parts by weight
Boric acid	5-30 parts by weight
Werner complex compound	0.3-1.8 parts by weight

This improved composition is disclosed and claimed in Du Pont's US Patent 2,723,212.

Du Pont markets several Werner type complexes under the trade name of "Quilon"® chrome complex.

OTHER USES

Additional uses in which ammonium sulfamate has shown promise include:—

- —fire retardant for sponge rubber
- —ingredient in rubber latex compositions
- —ingredient in dry cell batteries
- —stabilizer for pigments and zinc dust paints
- —glycerol and ammonium sulfamate as a dust collecting solution for use on air filters
- —in the preparation of phthalocyanine pigments

SAFE HANDLING

No hazards are encountered in the usual applications. Ammonium sulfamate in contact with the skin is neither very toxic nor very irritating. Ingestion causes irritant effects, but moderate doses appear to have no systemic toxic effects.

In 1962 the American Conference of Governmental Industrial Hygienists published a Threshold Limit Value of 15 mg per cubic meter of air for ammonium sulfamate. This concentration in air is intended to "represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect."

Support for this value is presented in Documentation of Threshold Limit Values by the American Conference of Governmental Industrial Hygienists (1962) as follows:

"(Ammonium sulfamate) has an acute oral LD_{50} of 3900 mg/kg for rats. It is thus improbable that acute or chronic poisoning can result from exposure to it under ordinary conditions of use.

*Sources, American Cyanamid Co.
Baird Chemical Industries, Inc., 15 W. 32nd St., N.Y.C.

"The Threshold Limit Value of (15 mg/m³) is assigned by analogy in the absence of inhalation toxicity data, and because several years of extensive use have apparently caused no illness."

At elevated temperatures the hydrolysis of ammonium sulfamate in water solution is fairly rapid. At 80°C a 10% solution will be 40-50% hydrolyzed in about 8 hours. In closed vessels and at higher temperatures a runaway hydrolysis reaction can occur which may end in explosion and rupture of the vessel. At reduced pH and higher concentrations this danger is enhanced, for example: a 60% solution at pH 2 will "runaway" at 130°C.

I.C.C. Label Requirements—none.

PACKAGING

Polyethylene lined multi-wall paper bags containing 100 lbs net weight and fiber drums containing 50 lbs net weight.

MATERIALS OF CONSTRUCTION

As with most salts, solutions of ammonium sulfamate are mildly corrosive to carbon steel. Stainless steel, lead, wood, glass, rubber-lined and ceramic vessels are generally suitable for handling and storage of ammonium sulfamate solutions. If mild steel must be used it is recommended that immediately after use all parts be flushed thoroughly with water.

SAN FRANCISCO, CALIF. 94119
P.O. Box 3200, Rincon Annex

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IN EUROPE
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A-31958

Furia, T.E., Ed. 1968
CRC Handbook of Food Additives
The Chemical Rubber Col, Cleveland,Ohio
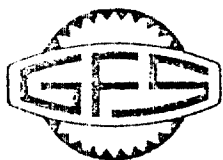
G. FREDERICK SMITH CHEMICAL COMPANY
867 McKinley Avenue, Columbus, Ohio 43223
614-224-5343

LOREN McBRIDE, Chemist

May 10, 1973

Mr. Donald W. Mc Kinstry
Tracor Jitco, Inc.
1300 E. Gude Drive
Rockville, Maryland 20851

Dear Mr. Mc Kinstry:

Thank you for your letter of May 2 regarding our Sulfamic Acid.
At present we purchase technical or commercial grade material
and purify it for primary standard and GFS Certified use. We
use no trade names or other common names for our product.
We list two grades of this material:

#97 Sulfamic Acid Primary Standard		#98 Sulfamic Acid GFS Certified
Assay	99.9%	99.97-100.03%
Insolubles	0.01%	0.01%
Heavy Metals	0.001%	0.001%
Iron	0.0005%	0.0005%
Chloride	0.001%	0.001%
Sulfate	0.05%	0.05%
Residue on ignition	0.01%	0.01%

Our products are not recommended for food, drug, or cosmetic use.

Very truly yours,

LM:FF

ANALYTICAL CHEMICALS SINCE 1928

Gleason, N.N., R.E. Gosselin, H.C. Hodge, and
R.P. Smith, 1969
Clinical Toxicology of Commercial Products, 3rd
edition
The Williams & Wilkins Co., Baltimore, Md.

Automatic Ion Exclusion–Partition Chromatography of Acids

G. A. HARLOW and D. H. MORMAN

Shell Development Co., Emeryville, Calif.

▶ A method has been developed for the automatic separation and determination of acids by ion exclusion–partition chromatography. Acids are separated on a column of a sulfonic acid ion exchange resin using only water as the eluent. The effluent is titrated automatically and the volume of titrant required is recorded as a function of time. The resulting integral curve indicates the quantity and possible identity of the individual acids. No pretreatment or regeneration of the column is required. Emergence data for over 50 acids of widely differing structure are presented relative to acetic acid. Apparatus which can be assembled from commercially available components is described.

DESPITE THE RECENT ADVANCES in nonaqueous titrimetry, many acid mixtures are still encountered which cannot be resolved by this means. Chromatographic methods have proved to be useful in separating many such mixtures. However, liquid chromatographic methods have not been widely used because the procedures which have been published usually involve the tedious collection and analysis of numerous individual fractions, a technique which is not very satisfactory for either routine or exploratory use.

This paper describes a method based on ion exclusion and partition chromatography, followed by automatic titration, which has proved to be very useful during the last four years in the resolution of mixtures of water soluble acids. Data are provided on the separability of various acids, and a procedure and automatic apparatus are described to make such separations convenient.

Wheaton and Bauman (*11*) first described ion exclusion separations. They also reported the application of the techniques of ion exclusion chromatography to the separation of nonionic materials (*10*). Simpson and Wheaton (*7*) examined the effects of varying the column parameters on column efficiency. However, ion exclusion has been described principally as a unit operation (*1, 6, 9, 11*) for process work. Analytical applications have been alluded to, but little information has been published to suggest what separations can be achieved by ion exclusion and by the same techniques applied to partition chromatography other than the deionization of nonelectrolytes.

Wheaton and Bauman (*11*) reported complete or partial resolution of the various pairs of acetic, chloroacetic, dichloroacetic, trichloroacetic, and hydrochloric acids, excepting the pair acetic–chloroacetic which were not separated despite their great difference in ionization constants. Reichenberg

(*4*), however, subsequently found that acetic acid could be almost completely separated from n-butyric acid although their pK's are almost identical. Thompson and Morris (*8*) investigated the separation of salts from amino acids by ion exclusion and extended the technique to the separation of amino acids from one another. Buchanan and Markiw (*2*) recently described the separations of a number of amino acids by what they called water elution chromatography on ion exchange resins. The method described here consists of separating the acids on a sulfonated polystyrene ion exchange resin in the hydrogen form using only water as the eluent. The column effluent is titrated automatically and the volume of titrant required is recorded as a function of time. The resulting integral curve gives the amount of each acid present and the emergence time indicates its possible identity.

The method has a number of attractive features to recommend it and compares favorably with gas chromatography in some respects. The procedure is extremely simple since it consists of passing the acids through a short column of ion exchange resin using only water as the eluent. No pretreatment of the resin is required since it is used in the acid form as supplied, and the resin may be used repeatedly without regeneration since, ordinarily, no ion exchange

occurs. Once the sample is placed on the column, the procedure is automatic and rapid, separation being achieved in less than an hour for most samples encountered. Since the detector is specific for acids, other materials generally do not interfere. The detector is absolute so calibration for individual acids is not required. Data are obtained directly in integral form simplifying calculation of results. The method is applicable to dilute aqueous solutions, and to strong mineral acids as well as water soluble organic acids, although the strong acids are not resolved from one another. The apparatus is simple and may be assembled from commercially available components.

The theory of ion exclusion has been discussed by Wheaton and Bauman (10, 11) and by Simpson and Wheaton (7). Reichenberg and Wall (5) have discussed the absorption of uncharged molecules by ion exchange resins. Briefly, the theory is as follows.

The resin bed consists of three parts: the solid resin network, the occluded liquid volume held within the resin beads, and the interstitial liquid volume between the resin particles. Although water is the only liquid used, the occluded liquid has a different character than the interstitial liquid because it is within a hydrocarbon matrix and contains a high concentration of ionic groups. The resin network thus serves as a boundary or semipermeable membrane between two liquid phases. Because of a Donnan membrane effect, highly ionized materials, like the strong mineral acids, are essentially excluded from the interior of the resin and pass through the column with the eluent front, emerging when the interstitial volume has been displaced. Nonionic materials, like most organic acids, are

free to enter the interior resin phase and thus emerge sometime later, after the interstitial plus the occluded liquid have been displaced. This separation of ionic from nonionic materials on an ion exchange resin is called ion exclusion.

In addition to this effect, there exist differences in the tendency of various nonionic materials to be retarded by the resin phase. These differences are due to both polar attractions between functional groups and to van der Waals forces between the nonelectrolytes and the hydrocarbon portion of the resin. The result is a partition of the solutes between the resin liquid and the interstitial liquid. This partition is described by the distribution coefficient, $K_d = C_r/C$, where C_r is the concentration of the solute in the liquid within the resin and C is the concentration of the solute in the liquid outside the resin. The ability to separate given solutes will depend on differences in K_d and will be affected by factors which affect K_d, such as the nature and concentration of the solute and the characteristics of the resin used.

EXPERIMENTAL

Apparatus. A diagram of the apparatus used for the automatic ion exclusion–partition chromatography of acids is shown in Figure 1. The effluent from the column enters the titration cell. When an acid emerges, the pH of the cell solution is lowered. The automatic titrator, which is set to maintain the solution at a pH of 8.5, senses the change through a combination glass-reference electrode. The unbalance created activates a relay in the automatic titrator which supplies power to the motor of the titrant syringe unit. The syringe delivers titrant (0.1N NaOH) to the cell which restores the solution pH to 8.5 at which point the

titrator stops the syringe drive. A potentiometer geared to the syringe drive provides a voltage output proportional to the syringe displacement and therefore proportional to the amount of acid eluted. This voltage is recorded as a function of time resulting in an integral curve as shown in Figure 2.

The titration assembly consists of a stand with a magnetic stirrer, a tall, narrow beaker with a miniature magnetic stirring bar, and an electrode holder with a combination pH electrode (Beckman No. 39142). The cell solution volume is kept at about 5 ml. by emptying occasionally during the blank periods between emerging acids in order to maintain good sensitivity and prevent the beaker from overflowing. A hypodermic syringe or vacuum flask is used for this purpose. A stream of nitrogen is maintained over the solution to avoid the absorption of CO_2.

The motor-driven syringe buret is of the type described by Lingane (3) and consists of a 5-r.p.m. Bodine synchronous motor geared to a threaded rod which pushes the syringe plunger. Also geared to the motor is a 10-turn Helipot. A mercury battery–potentiometer combination provides a suitable current so that the voltage drop across the Helipot at full syringe travel will give full-scale deflection on the potentiometric recorder. A limit switch is provided for the protection of the syringe. Titrant delivery may be varied by changing gears, syringe size, or titrant concentration.

A Brown stripchart recorder with a sensitivity of 2.5 mv. and a pen response of $4\frac{1}{2}$ seconds full scale is used. A chart speed of about 8 to 12 inches per hour is satisfactory.

The titration control unit is a Beckman Model K Automatic Titrator (Beckman Instruments, Inc., Fullerton, Calif.) without the delivery units and is used without modification. The motor-driven titrant syringe unit is connected to the normal delivery unit socket. A Radiometer TTT-1 Automatic Titrator (Radiometer, Copenhagen, Denmark, available from The London Co., Westlake, Ohio) has also been used but requires an additional relay since the control output is a d.c. voltage and the syringe drive motor requires a.c.

For normal use the ion exclusion column is a piece of borosilicate glass tubing 50 cm. long by 8-mm. o.d. with a hypodermic needle joint at the end. A 22-gauge hypodermic needle with Teflon tubing provides a flexible, low dead-volume connection to the titration cell. For applications where large sample sizes are required, a 100-cm. × 12-mm. column is used. The column is packed with analytical grade Dowex 50W-X12 ion exchange resin, 200- to 230-mesh, supplied by Bio-Rad Laboratories, Richmond, Calif. It is the hydrogen form of a sulfonic acid resin. Other grades than analytical may be used, but may require a long period of washing before a low blank is obtained. The column is filled by pouring in an aqueous slurry of the resin to avoid air bubbles.
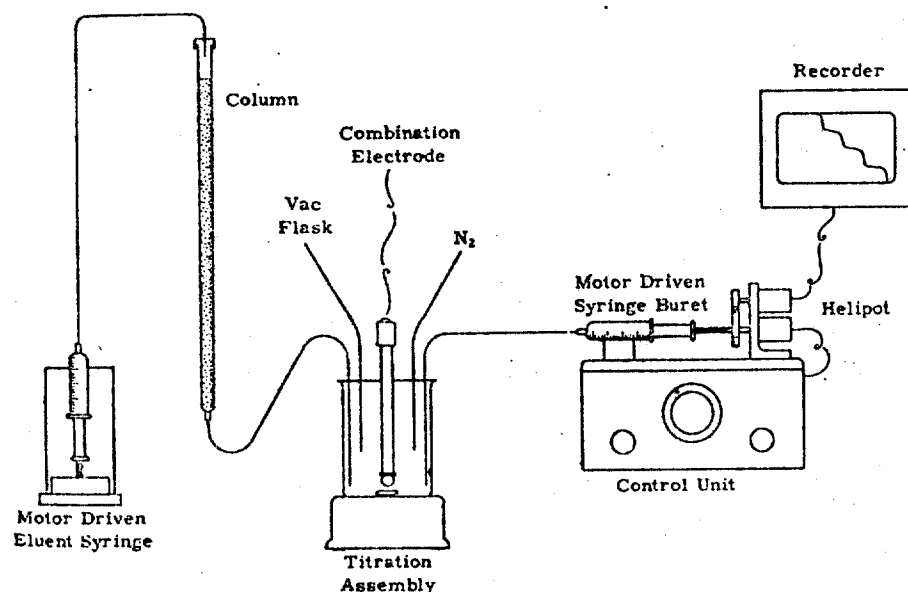

Figure 1. Apparatus for automatic ion exclusion–partition chromatography of acids
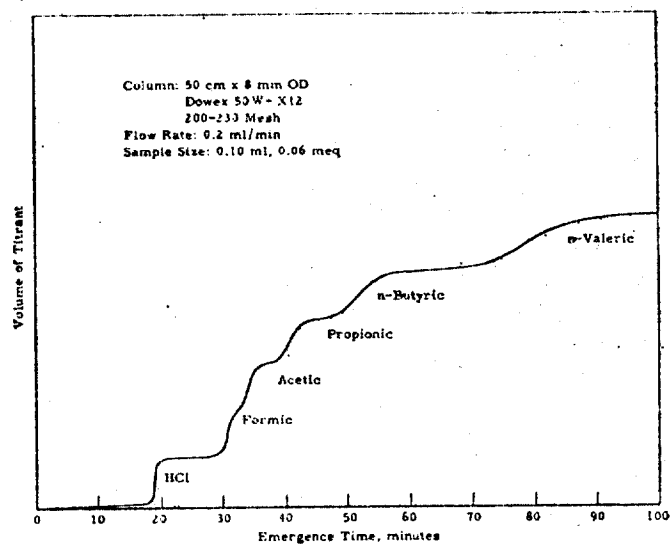
Figure 2. Automatic ion exclusion–partition chromatogram of a mixture of common acids
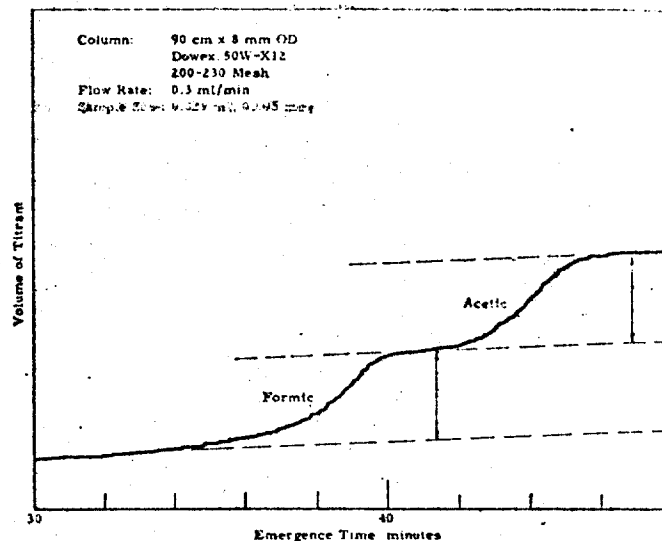

Figure 3. Separation of formic and acetic acids

The eluent, ion exchanged distilled water, is supplied to the column by a large motor-driven syringe of 20- to 100-ml. capacity. This provides a constant, reproducible flow rate which may be varied as required by changing gears and/or the syringe size. Connection is made to the top of the column with Teflon tubing and a hypodermic needle which pierces a rubber serum cap. An alternative method of controlling the eluent flow is by use of air pressure on a water reservoir bottle.

For laboratories which do not have facilities for building equipment, some alternatives to the above apparatus are commercially available. The Radiometer Titrigraph (Radiometer, Copenhagen, Denmark, available from The London Co., Westlake, Ohio) is very well suited for following the chromatographic separation of acids. It can be used without modification in the pH stat mode of operation and it is only necessary to provide the chromatographic column and eluent supply system.

There are a number of motor-driven syringes on the market. Some may possibly be modified for this use, but the authors are aware of only one which has an accessory available to provide an electrical output proportional to the syringe displacement. It is the Aminco Menisco-matic Buret (American Instrument Co., Silver Spring, Md.).

Choice of Parameters. A study was made of the various factors affecting resolution to achieve acceptable separations quickly on a convenient column. Initially, 100- to 200-mesh resin was used in a U-shaped column 2 meters long by 14-mm. o.d. At a flow rate of 1 ml. per minute, acetic acid emerged in about 60 minutes. A standard mixture of formic, acetic, and propionic acids was used to arrive at optimum column design and operating conditions.

One of the most significant factors in improving resolution was the use of finer resins with a narrow particle size range. A mesh size of 200 to 230 provided excellent resolution without excessive resistance to eluent flow. This permitted better separations in less time on much shorter columns. Shorter columns made it practical to use straight instead of U-shaped columns which also helped improve resolution. Reducing the column diameter to 8-mm. o.d. had little effect on resolution but did reduce the blank resulting from the slow release of strong acid from the resin and also decreased the eluent volume requirements. A flow rate of about 0.2 ml. per minute provided adequate resolution for most mixtures and gave an emergence time of about 35 minutes for acetic acid on a 50-cm. column.

Some comparisons were made of separations on resins with different degrees of crosslinkage. Dowex 50W–X12, with a high degree of cross-linkage, provided the best resolution of the weakly ionized organic acids and is preferred for general use. On the other hand, Dowex 50W–X2, with low cross-linkage, provided a greater separation of highly ionized acids like HCl from the organic acids and may be useful in some applications. For example, a mixture of formic, acetic, and chloroacetic acids can be resolved into only two components on Dowex 50W–X12 even by using a very small sample size and a low flow rate. However, on Dowex 50W–X2 under the same conditions, chloroacetic acid emerges faster resulting in the separation of all three acids.

Temperature might be expected to affect resolution by varying the rate of equilibration of the solute between the two phases. However, because of the fine particle size of the resin and the low flow rate, only a slight improvement was observed in the separation of formic, acetic, and propionic acids by increasing the column temperature from 0° to 50° C.

Small sample volumes and high concentrations favored good resolution as is true for chromatographic methods in general. For the 50-cm. × 8-mm. o.d. column described here, sample volumes less than 0.5 ml. and concentrations of about 0.5 to 1.0 meq. per milliliter are preferred. The sensitivity of the apparatus for normal operation is about 0.1 meq. for full-scale recorder deflection. This may be varied considerably by changing titrant concentration, syringe size, and/or the current through the Helipot. Maximum sensitivity is such that about 0.0002 meq. of acid can be detected.

Procedure. The initial water placed in the titration cell is titrated automatically to pH 8.5. The apparatus is calibrated in milliequivalents per millimeter chart deflection by introducing approximately 0.1 meq. of standard HCl into the titration beaker and titrating it automatically to pH 8.5. An appropriate aliquot of sample is then introduced directly into the cell and titrated automatically. This direct titration quickly indicates the proper sample size to use to obtain near full-scale deflection for the separation. It also serves to indicate whether any acids have not been recovered in the separation if the total deflection after separation is less than the direct titration, or whether there are salts present in the sample if the total deflection after separation is greater than the direct titration.

After the direct titration, the column effluent is directed into the cell. When a uniform base line is obtained, the eluent flow is stopped and the liquid level at the top of the column is brought just to the level of the resin bed. The sample is placed on the column with a pipet and forced just into the resin. Water is added to fill the column, the eluent flow is resumed, and the separation is recorded.

The chromatogram is calculated by measuring the height of each step between lines established parallel to the base line as shown in Figure 3. Results are then readily obtained for each acid in number of milliequivalents per milli-

liter or as per cent of the total acidity. A tentative identification can be made by comparison of the emergence times with those of known acids.

RESULTS

Relative Emergence Data. The emergence time of an acid is taken as the time at which one half of the acid has passed through the column. This time is a function of many factors such as flow rate, column length and temperature, packing, and the length of time a column has been in use. Therefore, the emergence of an acid is expressed as the ratio of its emergence time to that of some reference acid which has been chromatographed under the same conditions, a figure that remains relatively constant. Acetic acid has been chosen as a convenient reference.

Table I lists the emergence ratios with respect to acetic acid for over 50 acids of widely differing structure, ranging from 0.57 for very strong acids to 5.95 for benzohydroxamic acid. These ratios are generally good under a wide variety of conditions; however, the relative emergence of two acids can be altered by a change in sample concentration or volume since the distribution constant between phases may vary with concentration. The data in Table I, obtained with sample sizes of about 0.05 to 0.1 meq., do not necessarily hold exactly for very dilute solutions.

An idea as to the difference in emergence ratios required for the separation of two acids can be seen from Figure 2 which was obtained with a 50-cm. × 8-mm o.d. column of Dowex 50W-X12 and a flow rate of 0.2 ml. per minute. Formic acid (0.91) is not completely separated from acetic acid (1.00) under these conditions, but the pair can be completely resolved by using a smaller sample, lowering the flow rate, and/or increasing the column length as shown in Figure 3.

No definite correlations have been made between the emergence times of acids and any acid property. Such factors as ionization constant, water solubility, and molecular weight are important. A look at Table I leads to some generalizations based on a limited number of acids with widely varying structures and functional groups.

Strong acids, which are highly ionized, come through quickly with the eluent front. Mineral acids and sulfonic acids emerge first and are not separated from one another.

Amino acids do not emerge under conditions used for separating other acids. However, acids containing both an amino group and a sulfonic acid group—e.g., sulfamic, cysteic—emerge with the strong acids.

Table I. Emergence Data for Acids Relative to Acetic Acid by Ion Exclusion—Partition Chromatography

Acid	Ratio acid/acetic	Acid	Ratio acid/acetic
Sulfuric	0.57	Glutaric	1.0
Toluenesulfonic	0.57	Chloroacetic	1.0
Sulfurous	0.58	Acetic	1.00
5-Sulfosalicylic	0.58	Levulinic	1.0
Sulfamic	0.58	Nadic	1.0
Hydrochloric	0.59	L-Pyroglutamic	1.13
Acetylenedicarboxylic	0.59	Methylene-bis-mercapto-	
Trichloroacetic	0.60	acetic	1.15
Mucic	0.60	Propionic	1.17
L-Cysteic	0.61	Tetrahydrophthallic	1.21
Maleic	0.61–0.71	Acrylic	1.23
Oxalic	0.62	Carbonic	1.26
Phosphoric	0.63	Isobutyric	1.32
Citric	0.64	Butyric	1.45
Nitroform	0.67	Mandelic	1.49
Itaconic	0.70	Pivalic	1.49
Pyruvic	0.71	α-Hydroxybutyric	1.57
Malonic	0.72	Methacrylic	1.63
α-Ketobutyric	0.74	Isovaleric	1.66
Glyceric	0.75	Tertiary butylacetic	1.67
Boric	0.75–0.79	Crotonic	1.95
α-Ketovaleric	0.79	Valeric	2.09
Cyanuric	0.80	Furoic	2.09
Dichloroacetic	0.81	Cyclohexanecarboxylic	3.26
Mercaptosuccinic	0.82	2,4-Dihydroxybenzoic	3.80
Succinic	0.82	p-Hydroxybenzoic	4.46
Glycolic	0.82	Hydrocinnamic	5.40
Lactic	0.84	Benzohydroxamic	5.95
Formic	0.91		
Adipic	1.0		
Fumaric	1.0		

Members of a homologous series, like the aliphatic monocarboxylic acids, emerge in order of increasing molecular weight, decreasing acid strength, and decreasing water solubility.

Dibasic acids emerge faster than the monobasic acids of the same carbon number; oxalic acid emerges before acetic, and succinic before butyric.

An iso acid emerges before the corresponding normal acid; isobutyric precedes butyric, isovaleric comes before valeric, and methacrylic before crotonic.

A double bond retards an acid. Here is a case where a stronger acid may emerge later than the weaker acid; propionic (pK 4.87) emerges before acrylic (pK 4.26), and butyric (pK 4.82) precedes both crotonic (pK 4.70) and methacrylic (pK 4.66).

A keto group greatly speeds up the emergence of an acid relative to another of the same carbon number; α-keto-valeric acid greatly precedes valeric, and pyruvic emerges before propionic.

A hydroxyl group seems to have an unpredictable effect since glycolic acid emerges faster than acetic, but α-hydroxybutyric emerges later than butyric.

The substituted benzoic acids show strong retention. This may be due to a matrix effect accentuated by their low water solubility.

DISCUSSION

The technique described in this paper has proved useful in a number of applications other than the straightforward analysis of simple mixtures. Through the use of large columns, relatively large amounts of sample can be handled for the isolation of components for further identification by other analytical techniques or for the purpose of purification. The materials may be readily recovered as the free acids or as the corresponding sodium salts. Small amounts of acidic impurities in nonacidic materials may be determined by chromatographing a large amount of sample.

Small amounts of organic acids can be determined in the presence of a large excess of strong mineral acids by allowing the strong acids to be by-passed from the titration cell. Salts may be determined as the corresponding acids. Boric acid, which is normally too weak to titrate, may be determined by adding mannitol to the titration cell to form a complex which is a stronger acid. Esters may be determined by analysis of the saponified material. Acid anhydrides such as acetic and propionic readily hydrolyze on the column in the presence of the strong acid resin and may be determined without prior hydrolysis.

The main limitation of the method is

imposed by the requirement of water solubility for the sample. The use of elevated column temperatures might extend the usefulness of the technique to some acids which are poorly soluble in water at room temperature. Presently under investigation is the use of non-aqueous and mixed solvents.

ACKNOWLEDGMENT

Birdweil and D. A. Short obtained much of the data reported.

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Separation and Identification of Phenols in Automobile Exhaust by Paper and Gas Liquid Chromatography

ETHEL D. BARBER, EUGENE SAWICKI, and SYLVESTER P. McPHERSON

Laboratory of Engineering and Physical Sciences, Division of Air Pollution, Robert A. Taft Sanitary Engineering Center, Public Health Service, U. S. Department of Health, Education, and Welfare, Cincinnati, Ohio

▶ A method is described for the separation and identification of simple phenols in automobile exhaust by paper and gas liquid chromatography. Extended data are given on the separations in Crump's system on Schleicher and Schuell 2040A and 35 to 40% silica gel–impregnated 966 papers as well as separations on dimethylformamide-impregnated papers in dimethylformamide-hexane. The results of analysis of several samples by paper and gas liquid chromatography are presented.

HOFFMANN (5) has shown that phenols comprise a significant portion of the compounds found in automobile exhaust. Stanley et al. (8) and Smith (7) also have shown the presence of phenols in automobile exhaust. Because paper chromatographic methods have been used to identify phenols in many types of mixtures, it was considered worth while to attempt a study of phenols in automobile exhaust by this procedure. Of the various procedures tried, the most satisfactory was that of Crump (2), which uses the o- and p-nitro azo derivatives of phenols for paper chromatography. This study was complemented by gas chromatography of the pure phenols.

EXPERIMENTAL

Apparatus. Spectrophotometric measurements were made on a Cary Model 14 manufactured by Applied Physics Corp. Gas chromatographic analyses were made with a Perkin-Elmer Model 800 equipped with a differential hydrogen flame detector. Columns were made of stainless steel.

Reagents. Chemicals used, except where otherwise noted, were reagent grade. Phenols were freshly distilled or recrystallized. Known o-nitro-aniline derivatives were prepared according to Crump (2). Schleicher and Schuell paper 2040 A gl. and Schleicher and Schuell 35 to 40% silica gel-impregnated 966 were used for the paper chromatograms.

Procedure. Crump's system (2) of benzene-cyclohexane-dipropylene glycol (in the ratio of 30:70:3, v./v.) with papers impregnated with 20% formamide was used for separating phenols in which the 4 position is unsubstituted. Phenols in which the 4 position is substituted were separated on papers impregnated with 75% acetone–25% N,N-dimethylformamide (9) in the system N,N-dimethylformamide-hexane (1) in the ratio 20:80 v./v.

Determination of R_f Values. Solutions of pure o-nitrophenylazo dyes of approximately 1 mg. per ml. were chromatographed at 20° C. by the procedure of ascending chromatography (3, 4). The spots were visible and could be detected very easily with a white light. Some R_f values have been recorded by Crump (2) for a limited number of o-nitrophenylazo dyes in benzene-cyclohexane–dipropylene glycol on Whatman No. 1 paper. Table I records results for additional compounds and also presents values obtained for dyes in N,N-dimethylformamide-hexane.

Preparation of Automobile Exhaust Samples. Samples of raw automobile exhaust ranging from 3 to 5 cu. meters in volume were collected from an automobile mounted on a chassis dynamometer and operated under simulated driving conditions. The samples were collected in four Greenburg-Smith gas-type impingers connected in series. Three of the impingers contained 250 ml. of 0.1N to 1.0N sodium hydroxide solution at ice-water temperature; the fourth was a cold trap. The free phenols were released from the three impingers by adding hydrochloric acid to the sodium hydroxide solution until the solution was acidic. The solution in each impinger was extracted with two 100-ml. portions of chloroform. The fourth impinger was washed with 50 ml. of chloroform. From 50 to 70 ml. of the chloroform extract from each of the three impingers were combined and reacted with 25 ml. of 0.0105M diazotized o-nitroaniline. After thorough shaking, the mixture was allowed to stand for 2 minutes and was made alkaline by the addition of 25 ml. of sodium carbonate (20% by weight) (2). After acidification with dilute hydrochloric acid, the azo dyes were extracted with ether until all color was removed from the aqueous solution. The ethereal chloroform phase was dried over anhydrous magnesium sulfate and evaporated to dryness with a cool stream of air. The azo dye extract was dissolved in chloroform and made to a specific volume. A blank was prepared in the same manner as the sample. Chromatography was conducted as described above.

When the samples were collected in cold 1.0N sodium hydroxide solution, two impingers in series collected over 98% of the phenols with 95% in the first impinger. With 0.1N sodium hydroxide solution 95% of the phenols were collected in the two impingers with approximately two thirds in the first impinger.

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PATENT SPECIFICATION

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496,209

Complete Specification Left: April 25, 1938.

Complete Specification Accepted: Nov. 23, 1938.

PROVISIONAL SPECIFICATION

Improved Aqueous Solutions of Detergent Agents and Compositions comprising the same

We, JOHN GWYNANT EVANS, of Hexagon House, Blackley, Manchester, a British Subject, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a Company incorporated under the laws of Great Britain do hereby declare the nature of this invention to be as follows:—

Sulphonated oils, e.g. Turkey red oil, sulphonated oleic and ricinoleic acids and various derivatives thereof, soaps, sulphuric and other acid esters of higher fatty alcohols, and many other compounds for instance, oleyl-taurine, oleyl-isethionic acid, which can be described in general terms as having molecules which contain a fatty radical and a water-solubilising group together capable of forming an anion, and somewhat similar compounds obtained by sulphonating and alkylating naphthalene or suitable petroleum hydrocarbons, all possess properties which make them in varying degree adapted for use as detergent agents. That is to say, their aqueous solutions can be used with advantage over plain water for washing purposes.

We have found that the properties of aqueous solutions containing a detergent as above described are advantageously improved when there is present in the said aqueous solutions sulphamic acid, or imino-disulphonic acid or alkyl- or aryl sulphamic acids or the salts of these acids, such as the ammonium, sodium or potassium salts. For present purposes these will be known as sulphamic acid derivatives.

Accordingly the invention comprises the production of aqueous solutions of detergents and sulphamic acid derivatives as defined. The reagents may be added to the water or aqueous solution of other ingredients either simultaneously or successively, and it is a further feature of the invention to provide solid or pasty compositions adapted to give the said aqueous solutions by dissolving the same in water.

The aqueous solutions of the invention are intended to be used as baths for treating textiles.

It has been found that the speed with which detergents will dissolve in water is increased if there is present a sulphamic acid derivative. It has been found that the solubility is increased. It has been found that the surface active substances tend not to be precipitated by alkaline earth and heavy metals when sulphamic acid derivatives are present.

The invention is of particular interest in connexion with washing operations. Common soaps, as is well known, give precipitates, insoluble lime and magnesia soaps, in hard water. Even in dilute solutions sticky precipitates are formed. These precipitates adhere tenaciously to any textile material undergoing treatment. An adherent precipitate is also formed when hard water is used for rinsing laundered goods, in which rinsing process the earlier cleansing liquor is intended to be removed. When these precipitates remain in textile fibres, e.g. loose wool, or in laundered garments or other articles they adversely affect the handle and colour of the goods. Besides those washing operations for removing dirt from raw fibres or sullied goods, soaping treatments are given in the processing of dyed and printed goods in order to produce the most satisfactory shade and fastness properties. We refer, for instance, to the development or aftertreatment of dyeings of the so-called azoic colours. Before soaping the dyeing is usually of poor fastness to rubbing, chlorine and to light, and a soaping treatment is given to bring about an improvement in these properties. Moreover the first soaping treatment after coupling, if suitably carried out, alters the shade of the dyed material, in some cases considerably, whereas further soaping treatments have little or no effect. Consequently, in these cases, a soaping treatment is necessary if there is to be produced an article which can subsequently be described as fast to washing. Now if in these other soaping treatments the water used is hard and insoluble metallic soaps are formed on the dyed material they not only adversely affect the

finish but also diminish the fastness of the dyeing in various ways. If the azoic colours have been dyed on compact material, in the form of cops, there may have been irregular precipitation of lime soaps. Similar disadvantages of using soap and the given hard water together arise in the treatment of dyeings of vat dyestuffs.

Moreover, in the treatment of printed fabrics it is customary to give the materials a wash in a hot soap liquor to remove the thickening chemicals used in the application of the dyestuff, to remove surface colour and develop the final shade with full fastness properties. There again the deposition of lime soaps from hard water is an disadvantage. In addition there are often used in printing pastes ingredients which give alkaline earth or heavy metal ions and there form similarly objectionable insoluble metallic soaps.

By the present invention the above disadvantages of the use of soap together with hard water are overcome or diminished. Thus, the sulphamic acid derivatives are added to the soaping bath before or after the addition of the soap or they may be used in the rinsing liquors applied after the soaping operation.

The invention is illustrated but not limited by the following examples in which the parts are by weight, except in Example 5.

EXAMPLE 1.

To 1000 parts of water, 10 parts of the sodium salt of lauryl-3-sulpho-4-methoxy-aniline is added. The substance does not dissolve. 7.5 parts of ammonium iminodisulphonate are added. A clear solution is obtained.

Alternatively, 10 parts of the sodium salt of lauryl-3-sulpho-4-methoxy aniline and 7.5 parts of ammonium iminodisulphonate are mixed to give a dry powder, the whole of which dissolves smoothly and rapidly in 1000 parts of water. A clear solution of excellent detergent properties is thus obtained.

EXAMPLE 2.

10 parts of sodium salt of acid sulphuric ester of technical olein alcohol are dissolved in 1000 parts of water of 14° hardness (Clarke's Scale) at 60° C. The solution is not quite clear and separation takes place on cooling. To the solution 1 part of ammonium sulphamate is added. A comparatively clear solution is obtained and there is much less separation on cooling.

EXAMPLE 3.

10 parts of textile soap flakes are added to 1000 parts of hot water. This solution, if cooled to room temperature is liable to form a jelly, and hence be difficult to pump or feed by gravity through pipe lines. To the solution while still warm 1 part of ammonium sulphamate is added. When this solution is cooled it remains fluid.

A similar solution can of course be made from a prepared mixture of soap and ammonium sulphamate in the proportions of 10 parts of soap to 1 part of ammonium sulphamate or thereabouts.

EXAMPLE 4.

When scouring raw loose wool in water of 10° hardness in a four bowl machine, with a solution of sodium carbonate in the first bowl, sodium carbonate and soap in the second bowl, and soap alone in the third bowl, there is added to the fourth bowl, the so-called rinsing bowl sodium sulphamate at the rate of 2 parts per 1000 parts of liquor. After passage through these baths the wool is in a clean open condition free from deposited insoluble soaps.

EXAMPLE 5.

A load of 30 blankets is washed in a rotary machine as used in laundries using a mixture of

18 ozs. soap
6 ozs. sodium sesquicarbonate
2 ozs. sodium sulphamate in 80 gallons
water of 12° hardness

for 10 minutes at 100—110° F. After running off the liquor, a second wash is given with

12 ozs. soap
2 ozs. sodium sulphamate in 80 gallons
of water of 12° hardness

for 10 minutes at 100—110° F. The liquor is run off and the load given two rinses with water of 12° hardness at 100° F.

The blankets are in a clean condition, free from deposited lime soaps and have an attractive handle and colour.

Dated the 23rd day of April, 1937.
          E. C. G. CLARKE,
          Solicitor for the Applicants.

COMPLETE SPECIFICATION

Improved Aqueous Solutions of Detergent Agents and Compositions comprising the same

We, JOHN GWYNANT EVANS, of Hexagon House, Blackley, Manchester, a British Subject, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a Company incorporated under

the laws of Great Britain, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and
5 ascertained in and by the following statement:—

This invention relates to improved aqueous solutions of detergents, to compositions comprising the same, and parti-
10 cularly to such solutions and compositions which have been improved by the addition thereto of one or more salts of sulphamic acid or salts of a sulphamic acid derivative.
15 The detergents to which this invention relates are defined as water soluble compounds having molecules which contain a fatty radical and, a water-solubilizing group together capable of forming an
20 anion. There may be especially mentioned, as detergents, sulphonated oils. e.g. Turkey Red Oil, sulphonated oleic and ricinoleic acids and various derivatives thereof, soaps, sulphuric and other
25 acid esters of higher fatty alcohols, such as compounds of the general formula R—CO—X—R¹—SO₃H wherein X is O or NH, R¹ is a hydrocarbon radical e.g. alkylene or phenylene or substituted
30 phenylene and R is a fatty hydrocarbon radical. These compounds all possess properties which make them in varying degree adapted for use as detergent agents for treating textiles.
35 It is known that salts of the sulphamic acids obtained from the amines or carboxylic amides containing one or more open chain or cycloaliphatic radicals having at least 8 carbon atoms connected
40 with a nitrogen atom, or substitution products thereof, in conjunction with other detergent, wetting and emulsifying agents, may be employed with advantage as assistants in the textile, leather and re-
45 lated industries.

It is also known to use, to increase the capillary-active properties of aqueous solutions or emulsions, mixtures of water-soluble salts of phosphoric acids of lower
50 water content, than orthophosphoric acid, water-soluble salts of aromatic-sulphonic acids, together with at least one salt of a substituted or unsubstituted aliphatic or cycloaliphatic sulphamic acid contain-
55 ing at least six carbon atoms.

We have found that the properties of aqueous solutions containing a detergent as above defined are advantageously improved when there are present in the
60 said aqueous solution one or more salts of sulphamic acid, or of iminodisulphonic acid, or of a sulphamic acid of the general formula

$$\begin{array}{c} R^1 \\ \diagdown \\ \phantom{R^{11}}\diagup \\ R^{11} \end{array}\hspace{-1em}\diagup N—SO_3H$$
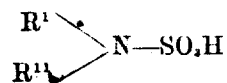
wherein R¹ may be hydrogen and R¹¹ or
65 both R¹ and R¹¹ may be alkyl radicals with not more than 4 carbon atoms, or wherein R¹ is hydrogen and R¹¹ is an aryl nucleus, which may be substituted only by an alkyl radical with not more than 4
70 carbon atoms, e.g. methylsulphamic acid, diethylsulphamic acid, phenylsulphamic acid or o- or p-tolylsulphamic acid. As suitable salts there may be used, for example, the ammonium, sodium or potas-
75 sium salts. For present purposes these salts will be known as sulphamic acid derivatives.

Accordingly the invention comprises
80 the production of aqueous solutions of detergents and sulphamic acid derivatives as defined. The reagents may be added to the water or aqueous solution of other ingredients either simultaneously or succes-
85 sively, and it is a further feature of the invention to provide solid or pasty compositions adapted to give the said aqueous solutions by dissolving the same in water.

The aqueous solutions of the invention
90 are intended to be used as baths for treating textiles.

It has been found that the speed with which detergents will dissolve in water is increased if there is present a sulphamic
95 acid derivative. It has been found that the solubility is increased. It has been found that the surface active substances tend not to be precipitated by alkaline earth and heavy metals when sulphamic
100 acid derivatives are present.

The invention is of particular interest in the prevention of the gelling of soap solutions. Soap solutions, except such as are of very low concentration, gel on
105 keeping unless they are stored at an elevated temperature. This limits the ways in which soap solutions may be employed or necessitates the use of special devices in order to avoid difficulties in the
110 technical manipulation of the solutions.

For example, in laundry washing practice it is commonly desired to maintain a stock solution of soap for use in the various washing operations. Convenient
115 strengths for such stock solutions (containing, for example, up to 10% of soap) are such that at ordinary temperatures they gel badly. To avoid gelation and to retain the solution in a form fit for use,
120 it must be kept hot. This in itself is not convenient and also is frequently the cause of further difficulty. For instance, when the heating is done by blowing steam directly into the solution, the
125 volume of liquid and hence the concentra-

tion of the solution, varies with the amount of steam used, so that there arise possibilities of error in the amount of soap used for any particular operation. Furthermore, in ordinary practice the stock solutions of soap are frequently to be conveyed from the place of storage to the place where they are actually used through pipe lines and in some cases the rate of addition of the soap solution to a washing machine may be controlled by delicate automatic feed devices. If stoppages occur in the pipe lines due to gelling of the soap solution, not only is there delay but there may also be risk of damage to the feed devices. For this reason also the stock soap solutions must ordinarily be kept hot.

In some cases it is not practicable to keep a soap solution hot and in such circumstances it is usual to employ special soaps or soap substitutes or to add other substances to the soap solutions, for example, alcohol, in order to avoid gelling difficulties. Where such additions are made, the proportion of the substances required to be added is relatively high.

These difficulties are avoided if there is added to the soap solution a small proportion of a sulphamic acid derivative as defined above; the necessity for using special soaps, for adding alcohol to the solution or for keeping the solution hot is thereby avoided, since even comparatively concentrated soap solutions which contain a small proportion of a sulphamic acid derivative do not gel on storage at room temperature.

The invention is also of interest in connection with washing operations in which trouble is experienced by reason of the formation of insoluble lime soaps. Common soaps, as is well known, give precipitates, insoluble lime and magnesia soaps, in hard water. Even in dilute solutions sticky precipitates are formed. These precipitates adhere tenaciously to any textile material undergoing treatment. An adherent precipitate is also formed when hard water is used for rinsing laundered goods, in which rinsing process the earlier cleansing liquor is intended to be removed. When these precipitates remain in textile fibres, e.g. loose wool, or in laundered garments or other articles they adversely affect the handle and colour of the goods. Besides those washing operations for removing dirt from raw fibres or sullied goods, soaping treatments are given in the processing of dyed and printed goods in order to produce the most satisfactory shade and fastness properties. We refer for instance, to the development or aftertreatment of dyeings of the so-called azoic colours. Before soaping the dyeing is usually of poor fastness to rubbing, chlorine and to light, and a soaping treatment is given to bring about an improvement in these properties. Moreover the first soaping treatment after coupling, if suitably carried out, alters the shade of the dyed material, in some cases considerably, whereas further soaping treatments have little or no effect. Consequently, in these cases, a soaping treatment is necessary if there is to be produced an article which can subsequently be described as fast to washing.

Now if in these other soaping treatments the water used is hard and insoluble metallic soaps are formed on the dyed material they not only adversely affect the finish but also diminish the fastness of the dyeing in various ways. If the azoic colours have been dyed on compact material, in the form of cops, there may have been irregular precipitation of lime soaps. Similar disadvantages of using soap and the given hard water together arise in the treatment of dyeings of vat dyestuffs.

Moreover, in the treatment of printed fabrics it is customary to give the materials a wash in a hot soap liquor to remove the thickening chemicals used in the application of the dyestuff, to remove surface colour and develop the final shade with full fastness properties. There again the deposition of lime soaps from hard water is a disadvantage. In addition there are often used in printing pastes ingredients which give alkaline earth or heavy metal ions and there form similarly objectionable insoluble metallic soaps.

By the present invention the above disadvantages of the use of soap together with hard water are overcome or diminished. Thus, the sulphamic acid derivatives are added to the soaping bath before or after the addition of the soap or they may be used in the rinsing liquors applied after the soaping operation.

The invention is illustrated but not limited by the following examples in which the parts are by weight, except in Example 5.

EXAMPLE 1.

To 1000 parts of water, 10 parts of the sodium salt of lauroyl-3-sulpho-4-methoxy-aniline is added. The substance does not dissolve. 7.5 parts of ammonium iminodisulphonate are added. A clear solution is obtained.

Alternatively, 10 parts of the sodium salt of lauroyl-3-sulpho-4-methoxy aniline and 7.5 parts of ammonium iminodisulphonate are mixed to give a dry powder, the whole of which dissolves smoothly and rapidly in 1000 parts of water. A clear solution of excellent detergent properties is thus obtained.

EXAMPLE 2.

10 parts of sodium salt of the acid sulphuric ester of technical olein alcohol are dissolved in 1000 parts of water of 14° hardness (Clarke's Scale) at 60° C. The solution is not quite clear and separation takes place on cooling. To the solution 1 part of ammonium sulphamate is added. A comparatively clear solution is obtained and there is much less separation on cooling.

EXAMPLE 3.

10 parts of textile soap flakes are added to 1000 parts of hot water. This solution, if cooled to room temperature is liable to form a jelly, and hence be difficult to pump or feed by gravity through the pipe lines. To the solution while still warm 1 part of ammonium sulphamate is added. When this solution is cooled it remains fluid.

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When scouring raw loose wool in water of 10° hardness in a four bowl machine, with a solution of sodium carbonate in the first bowl, sodium carbonate and soap in the second bowl, and soap alone in the third bowl, there is added to the fourth bowl, the so-called rinsing bowl sodium sulphamate at the rate of 2 parts per 1000 parts of liquor. After passage through these baths the wool is in a clean open condition free from deposited insoluble soaps.

EXAMPLE 5.

A load of 30 blankets is washed in a rotary machine as used in laundries using a mixture of

18 ozs. soap
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2 ozs. sodium sulphamate in 80 gallons water of 12° hardness

for 10 minutes at 100—110° F. After running off the liquor, a second wash is given with

12 ozs. soap
2 ozs. sodium sulphamate in 80 gallons of water of 12° hardness

for 10 minutes at 100—110° F. The liquor is run off and the load given two rinses with water of 12° hardness at 100° F.

The blankets are in a clean condition, free from deposited lime soaps and have an attractive handle and colour.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. An aqueous solution containing a detergent as hereinbefore defined and a sulphamic acid derivative as hereinbefore defined.

2. A solid or pasty composition capable of being dissolved in water to yield a solution claimed in Claim 2.

3. Detergent compositions substantially as described with reference to each of the foregoing Examples.

Dated the 25th day of April, 1938.

E. C. G. CLARKE,
Solicitor for the Applicants.

The significance of the R_M value in paper

chromatography of ammonia derivatives

of sulfuric acid

by

Gottfried Kempe

From: Institute of Inorganic Chemistry of the Technical College of
Chemistry, Leuna-Merseburg.

Martin (4), Bate-Smith and Westall (1), Reichl (5) and Schauer
and Bulirsch (6) have demonstrated the possibility of establishing
relationships between the R_f value and molecular structure. They
started out from the principle that for processes of distribution
in a state of equilibrium the change of the chemical potential is
equal to zero and that the maximum work A for the conversion of one
mol of the compound from one phase into another is made up roughly
additively of components of the individual groups of the molecule.

The R_M value introduced by Bate-Smith and Westall (1) plays
an important role and has the following connection with maximum work

$$A = kR_M - kP.$$

The R_M value, like the maximum work, is precisely made up
additively of so-called group constants,

$$R_M = mG_M + nG_N + \ldots Z,$$

in which the values m, n etc. give the frequencies of the groups M, N
etc. in the molecule. The basic constant Z contains the paper constant

P and the constant for the remaining molecular remnant after subtraction of the individual groups. According to Bate-Smith and Westall (1) the following relation exists between the R_M and the R_f value

$$R_M = \log \left(\frac{1}{R_f} - 1\right).$$

In the following we will use the R_M value defined by Reichl (5), which can be obtained from the above by multiplication by -1, which eliminates the discrepancy of high R_f values corresponding to negative R_M values and conversely:

$$R_M = \log \left(\frac{R_f}{1-R_f}\right).$$

Application to ammonia derivatives of sulfuric acid

The partially successful application of the R_M value to the calculation of R_f values from the molecular structure in homologous series of organic compounds by the above-mentioned authors led us to carry out similar studies on the ammonia derivatives of sulfuric acid.

These compounds can be well separated by the ascending method on Schleicher and Schüll paper no. 2043a with a vehicle consisting of 68.5 ml dioxane, 31.4 ml water, 0.1 ml concentrated NH_3 solution.

Detials of the development of the chromatograms have been reported elsewhere (2).

The substances applied as ammonium salts have the following R_f values at 20°C and a running time of ca. 16 hours.

Sulfate	H_2SO_4	0.18
Trisulfimide	$(HNSO_2)_3$	0.19
Sulfamide disulfonate	$SO_2(NH-SO_3H)_2$	0.29
Sulfamide monosulfonate	$H_2N-SO_2-NH-SO_3H$	0.39
Imidodisulfonate	$HN(SO_3H)_2$	0.54
Amidosulfonate	H_2N-SO_3H	0.66
Imidodisulfamide	$HN(SO_2-NH_2)_2$	0.78
Sulfamide	$SO_2(NH_2)_2$	0.91

These sulfur (VI)-nitrogen compounds, with the exception of the ring-shaped trisulfimide, can be regarded as members of three homologous series, of which the two first representatives are known:

A. Series of diamides $H(HN-SO_2)_nNH_2$

n = 1 sulfamide; n = 2 imidodisulfamide

B. Series of amido monosulfonic acids $H(HN-SO_2)_nOH$

n = 1 amidosulfonic acid; n = 2 sulfamide monosulfonic acid.

C. Series of disulfonic acids $HO_3S(HN-SO_2)_nOH$

n = 1 imidodisulfonic acid; n = 2 sulfamide disulfonic acid.

These series only differ from one another by the groups with which the $-HN-SO_2$ chains are saturated. These are the components of ammonia (A), water (B) and sulfuric acid (C). Every member of the homologous series differs from the previous one by the $-HN-SO_2$ group.

The chromatographic behavior of the compounds considered here allow the following qualitative conclusions to be drawn:

1. In a homologous series the next higher compound always has a lower R_f value than the previous one.

2. Corresponding members (the same n) of the three homologous series always travel so that the diamide has the highest and the disulfonic acid the lowest R_f value, while monosulfonic acid lies between the two. This is in accord with the fact that the sulfonic acid remnant is more hydrophile than the NH_2 group. The more sulfonic acid groups are contained in a compound, the more it tends to a stationary aqueous phase and the smaller its R_f value.

What qualitative relationships are there between the chemical constitution and the R_f values of the ammonia derivatives of sulfuric acid? As can be seen from Table 1, the R_M values of successive members of the three homologous series differ by the same amount.

This $\triangle R_M$ of -0.47 must be regarded as the constant G for the sulfimidogroup $-HN-SO_2-$. Since the members of all three series differ from one another by this group, starting out from any desired compound it is possible to determine the R_M and thus the R_f values of all other compounds of the series in question.

However, it is not possible to make a complete calculation of the R_f values from the molecular components, since for the constants of the four groups $-OH$, $-H$, $-NH_2$ and $-SO_2H$ (which, together with the $-NH-SO_2$ group, make up the individual molecules), and for the unknown basic constant Z only four independent equations can be written.

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It is to some extent possible, however, to determine differential amounts $\triangle R_M$ of the individual group constants and thus to produce relations between the corresponding members of various homologous series.

For instance the R_M values of the three compounds sulfamide, aminosulfonic acid and imidosulfonic acid are made up of the following quantities:

Sulfamide: $R_M(A) = G(-NH-SO_2-) + G(-H) + G(-NH_2) + Z$

Amidosulfonic acid: $R_M(B) = G(-HN-SO_2-) + G(-H) + G(-OH) + Z$

Imidodisulfonic acid: $R_M(C) = G(-NH-SO_2-) + G(-DO_3H) + G(-OH) + Z$

By subtraction we get

$R_M(AB) = R_M(B) = G(-NH_2) - G(-OH)$

$R_M(BC) = R_M(B) - R_M(C) = G(-H) - G(-SO_3H)$

These differential quantities must be added or subtracted in order to obtain the R_M values of the corresponding compounds of the two other homologous series, starting out from a random sulfur (VI)-nitrogen compound.

The following numerical values apply:

1. If the $-NH-SO_2$ member is added to a homologous series, The R_M value changes by -0.47.

2. Corresponding members (same n) of the homologous series A and B differ by the replacement of the OH group by the NH_2 group. A $\triangle R_M$ of 0.74 corresponds to this difference.

Replacement of $-NH_2$ by $-OH$ = -0.74

Replacement of $-OH$ by $-NH_2$ = 0.74.

3. Corresponding members (same n) of the homologous series B and C differ by the replacement of the H atom by the SO_3H group. This is manifested by a ΔR_M of 0.21.

Replacement of $-H$ by $-SO_3H$ = 0.21

Replacement of $-SO_3H$ by $-H$ = $+0.21$

The absence of the possibility to determine the basic constant, however, makes it necessary, when determining the R_M value, to start out from a firm reference value, for which the R_M value of amidosulfonic acid is appropriate, since this compound is the most readily accessible.

Table 2 shows the R_f values measured on 10 chromatrograms compared with those calculated according to the principle described here.

The calculation of the R_f values is of importance in so far that by this means it is possible to avoid the associated travel of other test substances (other than amidosulfonic acid) which are difficult of access. It is furthermore possible by this means to identify hitherto unknown substances in a mixture of substances. This method has its limits, however, as will be shown below.

Fig. 1 gives a graphic picture, on the one hand, of the calculated P_K values * of the first four to six members of each of the three homologous series, and on the other, the P_K values

measured on the chromatogram of a reaction product of unknown

composition.

---
*

In this figure P_K values were used which had been shown by experience to be more readily reproducible. They have the following connection with the R_f values:

$$P_S = \frac{R_f \text{ of the compound } . \ 100}{R_f \text{ of amidosulfonic acid.}}$$

It is apparent from the figure that by superposition of the three homologous series the more highly condensed ammonia derivatives of sulfuric acid are so strongly pressed together in the lowest part of the chromatogram that often there is no longer separation into individual spots. But even if this is the case, the difficulty of identification remains, which can no longer take place simply on the basis of the R_f, as can be seen from the diagram. However, there is some success in that a hitherto unknown compound in the conversion products of SO_2Cl_2 or $S_2O_5Cl_2$ with NH_3, concerning which a report has already been published elsewhere (3), can be identified with a strong degree of probability on the basis of its calculated R_f value. This is the diimidodisulfamide, $SO_2(NH-SO_2-NH_2)_2$, the next higher homolog of imidodisulfamide. This substance can be expected in both conversion products in notable quantities according to the presumed course of the reaction. The spot of substance lay directly beneath that of imidodisulfonate (see also Fig. 1). The deviations of the R_f values found from the calculated value were 0.01 at the most. Since this compound could not so far be visualized or isolated, proof ot its identity still remains to be furnished.

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It is also pointed out that calculation of the R_f value for ammonia derivatives of sulfuric acid is not possible for any random vehicle, since the R_f values of some compounds are strongly dependent upon the NH_3 content of the elution phase, while others are not. The reason for this is probably that the chemical nature of individual molecular groups, for example the NH group, differs in the compounds considered here.

Summary

Starting out from the R_f value of amidosulfonic acid it is possible to calculate the R_f values of all other chain-condensed ammonia derivatives of sulfuric acid. In the case of di-imidodisulfamide the substance could be identified with a strong degree of probability with the aid of the calculated R_f value, but in the case of longer chains the procedure is rendered virtually impossible due to the strong accumulation of compounds in the lower part of the chromatogram.

Tables

1. Group constant $\triangle R_M$ for $-SO_2-NH-$ as the difference in the R_M values of successive members of homologous series. Key: 1. Compound.

2. Differences between measured and calculated R_f values from 10 experiments. Key: 1. calculated. 2. measured.

Figure

1. Calculated and found P_K values of sulfur (VI)-nitrogen compounds. A. measured P_K values: x known compounds; ϕ unknown compounds; $\odot$ diimidodisulfamide. B. Calculated P_K values: o di-amides; $\circ$ monosulfonic acids; $\wedge$ disulfonic acids. Key: 1. P_K value.

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Author's address: Dr. Gottfried Kempe, Technische Hochschule für
Chemie Leuna-Merseburg, Merseburg, Geusaerstrasse.

Aus dem Institut für Anorganische Chemie der Technischen Hochschule für Chemie
Leuna-Merseburg

Die Bedeutung des R_M-Wertes
für die Papierchromatographie der Ammoniakderivate
der Schwefelsäure

Von

Gottfried Kempe

Mit 1 Textabbildung

(Eingegangen am 2. Dezember 1960)

In ihren Arbeiten haben Martin[4], Bate-Smith u. Westall[1], Reichl[5] sowie Schauer u. Bulirsch[6] Möglichkeiten aufgezeigt, Beziehungen zwischen dem R_f-Wert und der Molekülstruktur herzustellen. Sie gehen dabei von der Überlegung aus, daß für Verteilungsprozesse im Gleichgewichtszustand die Änderung des chemischen Potentials gleich Null ist, und daß die maximale Arbeit A für die Überführung eines Mols der Verbindung von der einen Phase in die andere sich näherungsweise additiv aus Anteilen für die einzelnen Gruppen des Moleküls zusammensetzt.

Dabei spielt der von Bate-Smith u. Westall[1] eingeführte R_M-Wert eine bedeutende Rolle, der mit der maximalen Arbeit in folgendem Zusammenhang steht:

$$A = k R_M - k P.$$

Der R_M-Wert setzt sich genau wie die maximale Arbeit additiv aus sogenannten Gruppenkonstanten zusammen,

$$R_M = m G_M + n G_N + \ldots Z,$$

wobei die Zahlen m, n usw. die Häufigkeiten der Gruppen M, N usw. im Molekül angeben. Die Grundkonstante Z beinhaltet die Papierkonstante P sowie die Konstante für den verbleibenden Molekülrest nach Abzug der einzelnen Gruppen. Zwischen dem R_M- und R_f-Wert besteht nach Bate-Smith u. Westall[1] die Beziehung

$$R_M = \log\left(\frac{1}{R_f} - 1\right).$$

Im folgenden soll jedoch der von Reichl[5] definierte R_M-Wert verwendet werden, der aus dem obigen durch Multiplikation mit -1 hervorgeht, wodurch die Diskrepanz beseitigt wird, daß große R_f-Werte negativen R_M-Werten entsprechen und umgekehrt:

$$R_M = \log\left(\frac{R_f}{1-R_f}\right).$$

Anwendung auf die Ammoniakderivate der Schwefelsäure

Die teilweise erfolgreiche Anwendung des R_M-Wertes zur Berechnung von R_f-Werten aus der Molekülstruktur bei homologen Reihen organischer Verbindungen durch obengenannte Autoren war Anlaß dazu, auch für die Ammoniakderivate der Schwefelsäure derartige Untersuchungen durchzuführen.

Diese Verbindungen lassen sich auf Schl. & Sch.-Papier Nr. 2043a mit einem Fließmittel der Zusammensetzung Dioxan 68,5 ml, Wasser 31,4 ml, konzentrierte NH_3-Lösung 0,1 ml, nach der aufsteigenden Methode gut trennen.

Über die Entwicklung der Chromatogramme wurde bereits an anderer Stelle[2] berichtet.

Die als Ammoniumsalze aufgetragenen Substanzen haben bei 20° C und einer Laufzeit von etwa 16 Std folgende R_f-Werte:

Sulfat	H_2SO_4	0,18
Trisulfimid	$(HNSO_2)_3$	0,19
Sulfamiddisulfonat	$SO_2(NH-SO_3H)_2$	0,29
Sulfamidmonosulfonat	$H_2N-SO_2-NH-SO_3H$	0,39
Imidodisulfonat	$HN(SO_3H)_2$	0,54
Amidosulfonat	H_2N-SO_3H	0,66
Imidodisulfamid	$HN(SO_2-NH_2)_2$	0,78
Sulfamid	$SO_2(NH_2)_2$	0,91 .

Diese Schwefel(VI)-Stickstoffverbindungen kann man mit Ausnahme des ringförmigen Trisulfimids als Glieder dreier homologer Reihen auffassen, von denen jeweils die ersten beiden Vertreter bekannt sind:

A. Reihe der Diamide $H(HN-SO_2)_nNH_2$
$n = 1$ Sulfamid; $n = 2$ Imidodisulfamid.
B. Reihe der Amido-Monosulfonsäuren $H(HN-SO_2)_nOH$
$n = 1$ Amidosulfonsäure; $n = 2$ Sulfamidmonosulfonsäure.
C. Reihe der Disulfonsäuren $HO_3S(HN-SO_2)_nOH$
$n = 1$ Imidodisulfonsäure; $n = 2$ Sulfamiddisulfonsäure.

Diese Reihen unterscheiden sich voneinander lediglich durch die Gruppen, mit denen die $-HN-SO_2$-Ketten abgesättigt sind. Es sind dies die Bestandteile des Ammoniaks (A), das Wassers (B) und der Schwefelsäure (C). Jedes Glied der homologen Reihe unterscheidet sich von dem vorangehenden durch die $-HN-SO_2$-Gruppe.

Das chromatographische Verhalten der hier betrachteten Verbindungen läßt zunächst folgende qualitative Aussagen zu:

1. In einer homologen Reihe hat die nächsthöhere Verbindung stets einen niedrigeren R_f-Wert als die vorhergehende.

2. Einander entsprechende Glieder (gleiches n) der drei homologen Reihen wandern stets so, daß das Diamid den höchsten, die Disulfonsäure den niedrigsten R_f-Wert hat, während die Monosulfonsäure

zwischen beiden liegt. Das steht damit in Einklang, daß der Sulfonsäurerest hydrophiler ist als die NH₂-Gruppe. Je mehr Sulfonsäuregruppen eine Verbindung enthält, um so mehr tendiert sie zur stationären wäßrigen Phase, um so kleiner ist ihr R_f-Wert.

Welche quantitativen Beziehungen bestehen zwischen der chemischen Konstitution und den R_f-Werten der Ammoniakderivate der Schwefel-

Tabelle 1. *Die Gruppenkonstante ΔR_M für $-SO_2-NH-$ als Differenz der R_M-Werte aufeinanderfolgender Glieder homologer Reihen*

Verbindung	R_f	R_M	ΔR_M ($-NH-SO_2-$)
Sulfamid	0,91	+ 1,02	} $-0,47$
Imidodisulfamid	0,78	+ 0,55	
Amidosulfonat	0,66	+ 0,29	} $-0,48$
Sulfamidmonosulfonat	0,39	− 0,19	
Imidodisulfonat	0,54	+ 0,07	} $-0,46$
Sulfamiddisulfonat	0,29	− 0,39	

säure? Wie aus Tab. 1 hervorgeht, unterscheiden sich die R_M-Werte aufeinanderfolgender Glieder der drei homologen Reihen um den gleichen Betrag.

Dieses ΔR_M von $-0,47$ muß als Konstante G für die Sulfimidogruppe $-HN-SO_2-$ angesehen werden. Da sich die Glieder aller drei Reihen durch diese Gruppe voneinander unterscheiden, ist es möglich, von einer beliebigen Verbindung ausgehend, die R_M- und damit die R_f-Werte aller anderen Verbindungen der betreffenden Reihe zu bestimmen.

Eine vollständige Berechnung der R_f-Werte aus den Molekülbausteinen ist jedoch nicht möglich, da für die Konstanten der vier Gruppen $-OH$, $-H$, $-NH_2$ und $-SO_3H$ (die zusammen mit der $-NH-SO_2-$ Gruppe die einzelnen Moleküle aufbauen) sowie für die unbekannte Grundkonstante Z nur vier unabhängige Gleichungen aufgestellt werden können.

Es ist jedoch möglich, gewissermaßen Differenzbeträge ΔR_M der einzelnen Gruppenkonstanten zu ermitteln, und somit Beziehungen zwischen entsprechenden Gliedern verschiedener homologer Reihen herzustellen.

So setzen sich z.B. die R_M-Werte der drei Verbindungen Sulfamid, Amido- und Imidodisulfonsäure aus folgenden Beträgen zusammen:

Sulfamid: $R_M(A) = G(-NH-SO_2-) + G(-H) + G(-NH_2) + Z$
Amidosulfonsäure: $R_M(B) = G(-NH-SO_2-) + G(-H) + G(-OH) + Z$
Imidodisulfonsäure: $R_M(C) = G(-NH-SO_2-) + G(-SO_3H) + G(-OH) + Z$.

Durch Subtraktion ergibt sich:

$$R_M(AB) = R_M(A) - R_M(B) = G(-NH_2) - G(-OH)$$
$$R_M(BC) = R_M(B) - R_M(C) = G(-H) - G(-SO_3H).$$

Diese Differenzbeträge müssen addiert bzw. subtrahiert werden, um von einer beliebigen Schwefel(VI)-Stickstoffverbindung ausgehend die R_M-Werte der entsprechenden Verbindungen der beiden anderen homologen Reihen zu erhalten.

Im einzelnen gelten dafür folgende Zahlenwerte:

1. Kommt in einer homologen Reihe das Glied $-NH-SO_2-$hinzu, so ändert sich der R_M-Wert um $-0,47$.

2. Entsprechende Glieder (gleiches n) der homologen Reihen A und B unterscheiden sich durch den Ersatz der OH-Gruppe durch die NH₂-Gruppe. Diesem Unterschied entspricht ein ΔR_M von 0,74.

$$\text{Ersatz von} -NH_2 \text{ durch} -OH = -0,74$$
$$\text{Ersatz von} -OH \text{ durch} -NH_2 = +0,74.$$

3. Entsprechende Glieder (gleiches n) der homologen Reihen B und C unterscheiden sich durch den Ersatz des H-Atoms durch die SO₃H-Gruppe. Das kommt in einem ΔR_M von 0,21 zum Ausdruck.

$$\text{Ersatz von} -H \text{ durch} -SO_3H = -0,21$$
$$\text{Ersatz von} -SO_3H \text{ durch} -H = +0,21.$$

Die fehlende Möglichkeit der Bestimmung der Grundkonstanten zwingt jedoch dazu, bei der Ermittlung der R_M-Werte von einer feststehenden Bezugsgröße auszugehen, als welche zweckmäßigerweise der R_M-Wert der Amidosulfonsäure dient, da diese Verbindung am leichtesten zugänglich ist.

In Tab. 2 sind die auf zehn Chromatogrammen gemessenen R_f-Werte mit dem nach dem hier dargelegten Prinzip berechneten verglichen.

Die Berechnung der R_f-Werte hat insofern Bedeutung, als dadurch auf das Mitlaufen von Testsubstanzen (außer Amidosulfonsäure) verzichtet werden kann, die zum Teil sehr schwer zugänglich sind. Es ist darüber hinaus möglich, in einem Substanzgemisch bisher noch unbekannte Substanzen zu identifizieren. Doch hat diese Methode, wie im folgenden gezeigt werden soll, ihre Grenzen.

Abb. 1 zeigt in graphischer Darstellung einmal die berechneten P_K-Werte* der ersten vier bis sechs Glieder jeder der drei homologen Reihen, zum anderen die P_K-Werte, die auf dem Chromatogramm eines Reaktionsproduktes unbekannter Zusammensetzung gemessen wurden.

Aus der Abbildung geht hervor, daß durch die Überlagerung der drei homologen Reihen die höherkondensierten Ammoniakderivate der

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* In dieser Darstellung wurden die P_K-Werte benutzt, die sich erfahrungsgemäß als besser reproduzierbar erwiesen. Mit den R_f-Werten stehen sie in folgendem Zusammenhang:

$$P_K = \frac{R_f \text{ der Verbindung} \cdot 100}{R_f \text{ der Amidosulfonsäure}}$$

Tabelle 2. *Differenzen zwischen den gemessenen und berechneten R_f-Werten aus zehn Versuchen* ($\Delta R_f = R_{f\,ber.} - R_{f\,gem.}$)

NH₄-SO₃H	SO₂(NH₂)₂			HN(SO₃H)₂			H₂N-SO₂-NH-SO₃H			HN(SO₃H)₂			SO₂(NH-SO₂)H		
gem.	gem.	ber.	ΔRf	gem.	ber.	ΔRf	gem.	ber.	ΔRf	gem.	ber.	ΔRf	gem.	ber.	ΔRf
0,67	0,91	0,92	+0,01	0,79	0,79	0,00	—	0,41	—	0,56	0,56	0,00	0,29	0,30	+0,01
0,65	0,89	0,90	+0,01	0,76	0,77	+0,01	—	0,39	—	0,54	0,54	0,00	0,29	0,28	—
0,68	0,93	0,92	—	0,80	0,80	0,00	0,40	0,42	+0,02	0,55	0,57	+0,02	0,31	0,31	0,00
0,69	0,93	0,93	+	0,80	0,81	+0,01	—	0,43	—	0,56	0,58	+0,02	0,30	0,32	+0,02
0,72	0,93	0,94	+0,01	0,82	0,82	0,00	0,41	0,46	+0,05	0,59	0,61	+0,02	0,31	0,35	+0,04
0,64	0,91	0,91	0,00	0,75	0,77	+0,02	0,38	0,37	+0,01	0,52	0,52	0,00	0,27	0,27	0,00
0,68	0,91	0,92	+0,01	0,78	0,80	+0,02	0,42	0,42	0,00	0,55	0,57	+0,02	0,30	0,31	+0,01
0,66	0,90	0,91	+0,01	0,78	0,78	0,00	0,39	0,40	+0,01	0,55	0,55	0,00	0,29	0,28	-0,01
0,69	0,93	0,93	0,00	0,80	0,81	+0,01	0,41	0,43	+0,02	0,56	0,58	+0,02	0,31	0,32	+0,01
0,64	0,91	0,91	0,00	0,77	0,77	0,00	0,42	0,37	-0,05	0,55	0,52	-0,03	0,27	0,27	0,00

Schwefelsäure im untersten Teil des Chromatogramms so stark zusammengedrängt werden, daß oft eine Trennung in einzelne Flecke
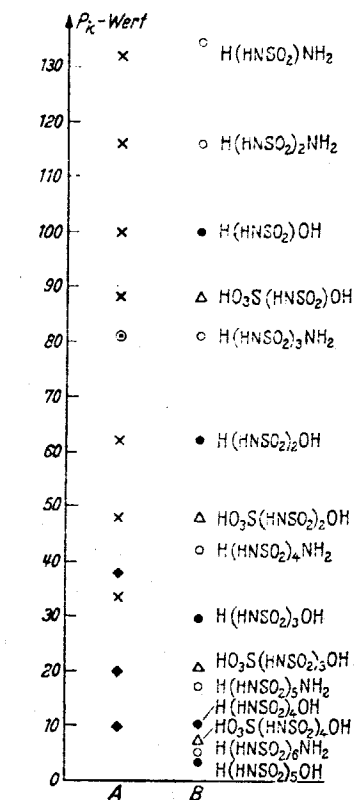

Abb. 1. Berechnete und gefundene P_K-Werte der Schwefel(VI)-Stickstoffverbindungen. *A* Gemessene P_K-Werte: × bekannte Verbindungen; ♦ unbekannte Verbindungen; ⊙ Diimidodisulfamid. *B* Berechnete P_K-Werte: ○ Diamide; ● Monosulfonsäuren; ▲ Disulfonsäuren

nicht mehr erfolgt. Aber selbst, wenn das noch der Fall ist, bleibt die Schwierigkeit der Identifizierung, die nicht mehr ohne weiteres an Hand der R_f-Werte erfolgen kann, wie aus dem Diagramm

ersichtlich ist. Ein Erfolg ist jedoch darin zu sehen, daß eine bisher unbekannte Verbindung in den Umsetzungsprodukten von SO_2Cl_2 bzw. $S_2O_5Cl_2$ mit NH_3, worüber schon an anderer Stelle berichtet wurde[3], mit großer Wahrscheinlichkeit an Hand ihres berechneten R_f-Wertes identifiziert werden konnte. Es handelt sich dabei um das Diimidodisulfamid, $SO_2(NH-SO_2-NH_2)_2$, das nächsthöhere Homologe des Imidodisulfamids. Diese Substanz ist auf Grund des angenommenen Reaktionsverlaufes in beiden Umsetzungsprodukten in nennenswertem Maße zu erwarten. Der Substanzfleck lag direkt unter dem des Imidodisulfonats (siehe auch Abb. 1), die Abweichungen der gefundenen R_f-Werte vom berechneten Wert betrugen maximal 0,01. Da diese Verbindung bisher noch nicht dargestellt bzw. isoliert werden konnte, muß der Beweis für die Identität noch erbracht werden.

Es sei jedoch anschließend noch darauf hingewiesen, daß eine Berechnung der R_f-Werte für die Ammoniakderivate der Schwefelsäure nicht für jedes beliebige Fließmittel möglich ist, da die R_f-Werte einiger Verbindungen stark vom NH_3-Gehalt der Elutionsphase abhängig sind, andere dagegen nicht. Der Grund hierfür muß darin gesehen werden, daß der chemische Charakter der einzelnen Molekülgruppen, beispielsweise der NH-Gruppe, in den hier betrachteten Verbindungen doch unterschiedlich ist.

Zusammenfassung

Vom R_f-Wert der Amidosulfonsäure ausgehend ist es möglich, die R_f-Werte aller anderen kettenförmig kondensierten Ammoniakderivate der Schwefelsäure zu berechnen. Im Falle des Diimidodisulfamids konnte eine Identifizierung der Substanz mit Hilfe des berechneten R_f-Wertes mit großer Wahrscheinlichkeit erfolgen, bei längeren Ketten wird dieses Verfahren jedoch infolge der starken Anhäufung von Verbindungen im unteren Teil des Chromatogramms nahezu unmöglich gemacht.

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Dr. GOTTFRIED KEMPE, Technische Hochschule für Chemie Leuna-Merseburg, Merseburg, Geusaer Straße

CHEMICALS IN FOODS: A REPORT TO THE ASSOCIATION OF FOOD AND DRUG OFFICIALS ON CURRENT DEVELOPMENTS. PART II. PESTICIDES

ARNOLD J. LEHMAN, M.D.

Chief, Division of Pharmacology, U. S. Food and Drug Administration

INTRODUCTION

The pesticides will be discussed under the sectional headings of acute toxicity, dermal toxicity, subacute and chronic toxicity, biochemistry, and pathology. In the tabular summaries to follow it will be necessary to mention many of the individual pesticides a number of times. Since their chemical names are too cumbersome for this purpose the common or short-term designation will be given preference. A list of the pesticides to be considered is given below. In this listing the short term is given first with the more customary chemical designation, wherever applicable, presented in the second column. Because of the diversified character of the pesticides from both the chemical and utility standpoint, a classification based upon either one or the other of these aspects did not appear to be practical; hence, in an attempt to segregate the compounds into some useful order an arrangement was devised which is based partially upon chemical similarity and partially upon use. Chemical names will not be repeated in tabulations and the groupings as presented below will be maintained.

Plant Products and Derivatives

1. Derris	Rotenone and rotenoids
2. Rotenone	
3. Pyrethrins	Oleoresins
4. Allethrin	Allyl cinerin
5. Nicotine	
6. Sabadilla	Veratrine-like alkaloids
7. Ryania	Alkaloids: ryanodine, ryanine, and others
8. Dihydrorotenone	

Thiocyanates

9. Thanite	Isobornyl-thiocyano acetate
10. Lethane-60	Beta-thiocyano-ethyl esters of aliphatic acids with 10–18 carbon atoms
11. Lethane-384	Beta-butoxy-beta-thiocyano-diethyl ether
12. Lethane Special	Lethane-60, 3 parts and Lethane-384, 1 part

Copper

13. Copper chloride	
14. Copper carbonate	
15. Copper sulfate	

Mercury

16. Calomel	Mercurous chloride
17. Corrosive sublimate	Mercuric chloride

18. Ethyl mercuric phosphate
19. Phenyl mercuric triethanol ammonium lactate

Arsenic

20. Arsenic trioxide
21. Potassium arsenite
22. Paris green   Copper aceto-arsenite
23. Calcium arsenate
24. Lead arsenate

Fluorides

25. Barium fluosilicate
26. Cryolite   Sodium aluminum fluoride
27. Sodium fluoride
28. Sodium fluosilicate

Miscellaneous Metals

29. Sodium selenite or selenate
30. Cadmium chloride
31. Tartar emetic   Potassium antimonyl tartrate

Chlorinated Hydrocarbons

32. DDT   Dichloro-diphenyl-trichloroethane
33. TDE   Dichloro-diphenyl-dichloroethane
34. DFDT   Difluoro-diphenyl-trichloroethane
35. Methoxychlor   Dimethoxy-diphenyl-trichloroethane
36. TBH   Technical benzene hexachloride
37. ABH   Alpha isomer of benzene hexachloride
38. BBH   Beta isomer of benzene hexachloride
39. DBH   Delta isomer of benzene hexachloride
40. Lindane   Gamma isomer of benzene hexachloride
41. Toxaphene   Chlorinated camphene
42. Chlordane   1,2,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexa-hydro-4,7-methanoindene
43. Aldrin   1,2,3,4,10,10 - Hexachloro - 1,4,4a,5,8,8a - hexahydro-1,4,5,8-dimethanonaphthalene
44. Dieldrin   1,2,3,4,10,10 - Hexachloro - 6,7 - epoxy - 1,4,4a,5,6,7,8,8a - octahydro - 1,4,5,8 - dimethanonaphthalene
45. Heptachlor   1,4,5,6,7,8,8 - Heptachloro - 3a,4,7,7a - tetra-hydro-4,7-methanoindene
46. Prolan   2-Nitro-1,1-bis(p-chlorophenyl) propane
47. Bulan   2-Nitro-1,1-bis(p-chlorophenyl) butane

Organic Phosphates

48. Parathion   O,O-Diethyl-p-nitrophenyl-thiophosphate
49. Dimethyl parathion   O,O-Dimethyl-p-nitrophenyl-thiophosphate
50. Paraoxone   O,O-Diethyl-p-nitrophenyl-phosphate
51. OMPA   Octamethyl pyrophosphoramide
52. EPN   Ethyl p-nitrophenyl-thionobenzenephosphonate
53. TEPP   Tetraethylpyrophosphate
54. HETP   Hexaethyltetraphosphate
55. ASP-47   Tetraethyldithionopyrophosphate

56. E-838	Diethoxythiophosphoric acid ester of 7-hy-droxy-4-methyl-coumarin

Dinitro Compounds

57. DNOC	3,5-Dinitro-o-cresol
58. DN-111	2,4-dinitro-o-cyclohexyl phenol dicyclohexyl-amine

Herbicides

59. 2,4-D	2,4-Dichlorophenoxy acetic acid
60. 2,4,5-T	2,4,5-Trichlorophenoxy acetic acid
61. Naphthalene acetic acid	
62. Methyl-1-naphthalene acetic acid	
63. Ammate	Ammonium sulfamate
64. Pentachlorophenol	
65. Endothal	3,6-Endoxohexahydrophthalic acid
66. Maleic hydrazide	

Activators

67. n-Propyl-isome	di - n - Propyl - 6,7 - methylenedioxy - 3 - methyl - 1,2,3,4 - tetrahydronaphthalene - 1,2-dicarboxylate
68. Piperonyl butoxide	(Butylcarbityl) (6-propyl piperonyl) ether
69. Van Dyke 264	n-Octyl-bicycloheptane dicarboximide
70. Sulfoxide	n-Octyl-sulfoxide
71. Piperonyl cyclohexanone	Alkyl-5-(3,4-methylenedioxy)-phenyl-3-3-cyclo-hexen-5-one

Rodenticides

72. 1080	Sodium monofluoroacetate
73. Castrix	2-Chloro-4-dimethylamino-6-methylpyrimidine
74. ANTU	Alpha-napbthylthiourea
75. Warfarin	2 - Alpha - phenyl - beta - acetyl - ethyl - 4 hydroxy-coumarin
76. Strychnine	Strychnine nitrate
77. Thallium sulfate	
78. Red squill	
79. Zinc phosphide	

Miscellaneous

80. Phygon	2,3-Dichloronaphthaquionne
81. Spergon	Tetrachlorobenzoquinone
82. Phenothiazine	Thiodiphenylamine
83. Aramite	Beta' - chloroethyl - beta - (p - tert. - butyl - phenoxy)-alpha-methyl-ethyl sulfite
84. Arasan	Tetramethyl-thiuram-disulfide
85. Fungicide 341 C	Glyoxalidine acetate
86. Dithane	Zinc and sodium salts of ethylene-bis-dithio-carbamic acid

SECTION I. ACUTE ORAL TOXICITY

The acute toxic dose values for the pesticides are listed in Table I. Practically all of the data were obtained in the laboratories of the Division

of Pharmacology, and, with a very few exceptions, the rat was employed as the test animal. The values for a few of the older compounds such as derris, sodium fluoride, and arsenic trioxide are so well documented in the literature that they were not necessarily checked in this laboratory. In some instances technical difficulties would not permit the calculation of an LD_{50}, hence, in the interest of accuracy the term "approximate LD_{50}" is given as the column heading. Wherever possible the pure compound dissolved in an innocuous solvent was employed, and dosages were administered by stomach tube to fasted animals.

In an attempt to present as much useful information as possible in tabular form, the chief characteristics of the poisoning symptoms, the time elements involved in their appearance and duration, and the clinical course of the poisoning as observed in the animals are briefly summarized. A few additional comments on the various groups of pesticides follow.

Thiocyanates: Except for thanite, the acute toxicity was determined on the commercially available concentrates which are 50% solutions in deodorized kerosene. The LD_{50}'s as tabulated were calculated on the basis of the pure compound.

Copper: Although the compounds listed are not used as pesticides, their toxicity does serve to give some estimation of the toxicity of copper oxychloride, oxide, phosphate, silicate, zeolite, oxychloridesulfate, and Bordeaux Mixture.

Mercury: The general trend of phenyl mercuric compounds is an LD_{50} of 50 mg./kg. or less.

Arsenic: The ratio of toxicity of arsenites to arsenates may be considered as 1:1.6; hence, other arsenical pesticides not listed, such as sodium and zinc arsenites, would have an LD_{50} of about 13–14 mg./kg., and copper, magnesium, and manganese arsenates would be in the 22–23 mg./kg. range.

Miscellaneous Metals: The value for sodium selenite or selenate is calculated on the basis of selenium. The toxic dose of cadmium chloride is listed because this metal is a constituent of at least one fungicide, a combination of cadmium copper zinc chromate and calcium sulfate.

TABLE I
Acute oral toxicity

PESTICIDE	APPROXI-MATE LD₅₀ Mg./Kg.	SYMPTOMS OF POISONING			
		Chief Characteristics	Onset	Duration	Clinical Course with Severe Poisoning
Natural products and derivatives					
1. Derris	1500	Frequent convulsive seizures followed by depression of central nervous system	Within minutes to 5 to 6 hours	1 to 3 days	Death by respiratory failure in 24 hours. Fatalities rare after 3rd day although death may be delayed 10 or 12 days
2. Rotenone	132	Same as for derris			Death may be delayed for as long as 5 days. Respiratory paralysis is a major cause of death
3. Pyrethrins	200	Central nervous system irritation; hyperexcitability, tremors, and convulsions	Usually within ½ hour	10 hours	
4. Allethrin	680	Tremors and convulsions	30 minutes	6 hours	Fatalities appear to be rare 24 hours after poisoning. Death due to respiratory paralysis
5. Nicotine	50–60	Clonic convulsions	Within minutes	5 to 20 minutes	Curare-like paralysis of respiratory muscles and death
6. Sabadilla	4000	Retching, muscular spasms, ataxia, coma	Within 5 minutes	24 hours	Symptoms similar to aconite. Death from respiratory or cardiac paralysis may occur within 3 to 10 minutes after the ingestion of a fatal dose

7. Ryania	750	Depression of central nervous system	5 to 8 minutes	2 to 10 hours	Continuous depression up to terminal convulsions. Death usually within 24 hours although large doses may be fatal within the hour after ingestion
8. Dihydrorotenone	330	Same as for derris			

<div align="center">Thiocyanates</div>

9. Thanite	1000	Deep depression, cyanosis, dyspnea and tonic convulsions	Within a few minutes	Rapid collapse within minutes	Occasionally symptoms may be delayed for a few hours. Death is due to respiratory paralysis
10. Lethane-60	500				
11. Lethane-384	90				
12. Lethane Special	400				

<div align="center">Copper</div>

13. Copper chloride	140	Violent retching, muscular spasms and collapse	Within a few minutes	If dose is retained could be fatal in 1 hour	Symptoms of gastrointestinal irritation may subside, but death may follow several days later because of damage to important organs such as liver and kidneys
14. Copper carbonate	159				
15. Copper sulfate	300				

<div align="center">Mercury</div>

16. Calomel	(210)				Symptoms of mercurialism at this dose but no deaths
17. Corrosive sublimate	37	Shock, dysentery, and anuria	Immediate	Symptoms persist till death	Shock effect of the irritant may be fatal within 24 hours. Acute kidney damage may be fatal by the third day
18. Ethyl mercuric phosphate	30	Similar to corrosive sublimate			
19. Phenyl mercuric triethanol ammonium lactate	30				

TABLE 1—*Continued*

PESTICIDE	APPROXI-MATE LD₅₀ Mg./Kg.	SYMPTOMS OF POISONING			
		Chief Characteristics	Onset	Duration	Clinical Course with Severe Poisoning
ARSENIC					
20. Arsenic trioxide	13	Violent gastroenteritis, diarrhea, rice water stools	Almost immediately	A few hours to several days	Death from exhaustion and dehydration. Convulsions and general paralysis may occur before onset of gastroenteritis. Death within a few hours to several days
21. Potassium arsenite	14				
22. Paris green	22				
23. Calcium arsenate	20				
24. Lead arsenate	100				
Fluorides					
25. Barium fluosilicate	175	Abdominal distress, diarrhea, cyanosis, dyspnea, fibrillation of skeletal muscles	Immediately and up to 6 hours	Stupor and weakness may persist for 36 hours	In fatal poisonings death can result in a few minutes
26. Cryolite	200				
27. Sodium fluoride	200				
28. Sodium fluosilicate	125				
Miscellaneous Metals					
29. Sodium selenite or selenate	2.5	Garlic breath, nervousness, central nervous system depression	Within 15 minutes	12 to 18 hours	Death due to respiratory failure
30. Cadmium chloride	88	Salivation, vomiting, diarrhea	15 to 30 minutes		Gastroenteritis may be a contributing cause of death.
31. Tartar emetic	115	Parallels those given for arsenic poisoning			Death within a few hours to several days

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Chlorinated hydrocarbons

32. DDT	250	Extreme excitability, tremors, twitching, convulsions, coma, death	Within 30 minutes	24 hours	Time interval for a fatal outcome is variable, but death usually occurs within 24 hours
33. TDE	3400	Lethargy	Within 24 hours	2 to 4 days	Convulsions do not appear to be a major symptom. If death has not occurred by the 4th day prognosis appears to be favorable
34. DFDT	1120	Similar to DDT			Apparently the fluorine part of the molecule does not contribute to the symptoms of acute poisoning
35. Methoxychlor	6000	Largely depression of central nervous system	Within 24 hours	2 to 4 days	Tremors have been noted but are not a prominent symptom
36. TBH	600	Convulsions which may give way to a central nervous system depression	Within 20 minutes	2 weeks	Symptoms may persist for 2 weeks and deaths have been observed late in the 2 weeks observation
37. ABH	500	Hyperexcitability and convulsions	About 1 hour	2 weeks	Deaths delayed up to 2 weeks with convulsions persisting to the end
38. BBH	6000	Principally tremors	2 to 5 hours	2 days	Death occurs between the 2nd and 6th day
39. DBH	1000	Depressant to the central nervous system	1 to 2 hours	2 days	Death may be delayed to between the 2nd and 6th day

TABLE 1—*Continued*

PESTICIDE	APPROXI-MATE LD₅₀ Mg./Kg.	SYMPTOMS OF POISONING			
		Chief Characteristics	Onset	Duration	Clinical Course with Severe Poisoning
Chlorinated hydrocarbons—*Continued*					
40. Lindane	125	Hypersensitivity and convulsions	20 minutes	2 hours	Death usually within a two-hour period after ingestion. Convulsions persist to the end
41. Toxaphene	69	Hypersensitivity, tremors, and convulsions	1½ hours	24 hours	Most of the fatalities occur within 24 hours. Delayed deaths have been noted up to the 6th day
42. Chlordane, technical	457	Hypersensitivity, tremors, and convulsions	15 minutes	2 days	Tremors begin in 15 minutes; convulsions appear after about 24 hours and may persist for 2 days; deaths may be delayed up to the 6th day
43. Aldrin	67	Tremors and convulsions	Within 1 hour	2 days	Time of death variable; may be delayed up to the 6th day
44. Dieldrin	87	Tremors, muscular spasms, convulsions	Usually within the hour	2 days	Deaths may be delayed up to the 6th day or longer
45. Heptachlor	90	Tremors and convulsions	30 minutes to an hour	2 days	Similar to aldrin, dieldrin and chlordane
46. Prolan	4000	Tremors and convulsions	Within about 1 hour	Prolonged for days	Persistent convulsions up to time of death which may not occur within 4 hours
47. Bulan	330	Convulsions	About 2 hours	4 hours	Fatalities usually occur within 4 hours

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Organic Phosphates

48. Parathion	3	Generalized fibrillary tremors, salivation, lacrimation, diarrhea and convulsions	15 minutes to 1 hour	12 hours	The symptomatology of the individual organic phosphates is similar. Deaths usually occur in 1 to 24 hours
49. Dimethyl parathion	15.2				
50. Paraoxone	7.8				
51. OMPA	13.5				
52. EPN	14.5				
53. TEPP	1.2				
54. HETP	7				
55. ASP-47	5				
56. E-838	19				

Dinitro Compounds

57. DNOC	26	Increased respiratory rate	Within the hour	24 hours	Time of death variable but usually within 24 hours with hyperpyrexia contributing cause
58. DN-111	330				

Herbicides

59. 2,4-D	500	Ataxia, myotonia, gastrointestinal irritation	30 minutes	Several hours	Death occurs several hours after ingestion
60. 2,4,5-T	300	Similar to 2,4-D			
61. Naphthalene acetic acid	1000	Gastroenteritis, depression and paralysis	30 minutes	Less than 24 hours	Most fatalities occur within the first 48 hours
62. Methyl-1-naphthalene acetic acid	2140				
63. Ammate	3900	Listlessness	Within minutes	24 hours	Tremors have been noted with very high doses and death within 10 minutes. Survival after 24 hours is favorable for complete recovery
64. Pentachlorophenol	78	Tremors and convulsions	20 minutes	12 hours	Deaths usually within the hour

TABLE 1—*Continued*

PESTICIDE	APPROXI-MATE LD₅₀ Mg./Kg.	SYMPTOMS OF POISONING			
		Chief Characteristics	Onset	Duration	Clinical Course with Severe Poisoning
Herbicides					
65. Endothal	35.5	Muscular weakness	30 minutes	24 hours	Deaths occurred between 4 and 24 hours
66. Maleic hydrazide	4000	Tremors, muscular spasms	10 to 60 minutes	3 hours	Deaths within 3 hours
Activators					
67. n-Propyl isome	15000	Depression			
68. Piperonyl butoxide	11500	Depression	20 minutes	Several days	Delayed deaths up to one week
69. Van Dyke 264	2800	Some hyperexcitability followed by depression	30 minutes	2 days	Most fatalities occur within the 2-day period
70. Sulfoxide	2000	Tremors, severe depression, coma	10 to 20 minutes	24 hours or more	Continuous severe depression till death. Survivals may have severe symptoms extending beyond the 24-hour period
71. Piperonyl cyclohexanone	5200				Death usually within three days
Rodenticides					
72. 1080	1.7	Tremors, convulsions	45 minutes	1 week	Intermittent convulsions for as long as 10 days before death
73. Castrix	1.7	Convulsions	45 minutes	12 hours	Survival for more than 12 hours appears to be a favorable prognostic sign
74. ANTU	6	Dyspnea; occasionally convulsions	15 minutes	24 hours	Death usually occurs within 24 hours

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75. Warfarin	160	Severe depression; generalized hemorrhages			Deaths are usually delayed but in severe poisoning death could occur within a half hour after ingestion
76. Strychnine	16.2	Tonic convulsions	10 minutes	12 hours	Deaths from medullary paralysis and exhaustion and usually occur within a 12-hour period
77. Thallium sulfate	25	Depression	48 hours	72 hours	Most of the fatalities occur within the 72-hour period. Renal damage is the principal cause
78. Red squill	300	Central nervous system stimulation	12 hours	24 hours	Animals exhibit circular movements; repeated rotation on long axis of body. Majority of deaths fall within the 24-hour period
79. Zinc phosphide	450	Depression	24 hours	72 hours	Most deaths occur within 72 hours
Miscellaneous					
80. Phygon	1500	Diarrhea and severe depression			Deaths occur within 24 hours
81. Spergon	4200	Depression			Depression may be prolonged for days before death
82. Phenothiazine	5000	Secondary anemia			Recovery from temporary secondary anemia if poisoning is not serious; no residual toxic effects
83. Aramite	6300	Depression	3 hours	3 days	Delayed deaths over 1 week
84. Arasan	865	Hyperexcitability, severe diarrhea			Most deaths occur within 5 days
85. Fungicide 341 C	3720	Depression, hemorrhage from the nose			Delayed deaths up to 2 weeks
86. Dithane	5000	Diarrhea			

pointed out that the relation may be equally well expressed by altering Rudolphi's formula into

$$K = \frac{\left(\frac{\mu_v}{\mu_\infty}\right)^3}{\left(1 - \frac{\mu_v}{\mu_\infty}\right)\sqrt{v}} = \frac{\left(\frac{\mu_v}{\mu_\infty}\right)^3}{\left(1 - \frac{\mu_v}{\mu_\infty}\right)^2 v} = \frac{\left(\frac{\mu_v}{\mu_\infty} \cdot \frac{1}{v}\right)^3}{\left\{\left(1 - \frac{\mu_v}{\mu_\infty}\right)\frac{1}{v}\right\}^2},$$

which may be written as

$$K = C_i^3/C_s^2,$$

where $\dfrac{\mu_v}{\mu_\infty} \cdot \dfrac{1}{v} = C_i$ is the concentration of the ion, and

$$\left(1 - \frac{\mu_v}{\mu_\infty}\right)\frac{1}{v} = C_s$$

is that of the undissociated salt. I have tested the above formulæ with sodium amidosulphonate; the results which are tabulated below are in agreement with both of them:

Sodium Amidosulphonate ($\mu_\infty = 98\cdot17$).

v	$= 32$	64	128	256	512	1024
μ_v	$= 84\cdot25$	$87\cdot79$	$90\cdot52$	$92\cdot04$	$93\cdot90$	$94\cdot51$
K_R	$= 1\cdot00$	$1\cdot03$	$1\cdot05$	$0\cdot96$	$1\cdot01$	$0\cdot85$
K_H	$= 1\cdot00$	$1\cdot01$	$1\cdot01$	$0\cdot92$	$0\cdot96$	$0\cdot80$

The values of K_R and K_H have been calculated according to Rudolphi's and van't Hoff's formulæ, respectively, the value found for $v = 32$ litres being, in both cases, made equal to 1. The results are almost equally constant up to $v = 512$ litres, but, in both cases, there is a greater deviation for the last dilution, owing, no doubt, to a greater experimental error.

CXII.—*Physiological Action of Amidosulphonic acid.*
By Oscar Loew, Ph.D.

At the suggestion of my colleague, Dr. Edward Divers, I have made a series of physiological tests on plants with amidosulphonic acid (amidosulphuric acid). This acid, in 0·05—0·1 per cent. solutions, was applied in the form of its calcium or sodium salt, either alone or in conjunction with mineral nutrient salts, namely, monopotassium phosphate, 0·05 per cent.; magnesium sulphate, 0·05 per cent.; calcium sulphate, 0·1 per cent.; and a trace of ferrous sulphate. These solutions (500 c.c.) were applied to the whole plants, or to the branches and isolated leaves, of different families of the phænogams; also to algæ, lower fungi, and lower aquatic animals.

The principal result, in regard to phænogams, was that amidosulphonic acid has, even in its salts, a *decidedly noxious action*, clearly established by control experiments, made at the same time and on similar organisms, kept in water and in solutions of ammonium sulphate and sodium sulphate. Some of the experiments were the following:

Young wheat plants, carefully taken from the field, 20—25 cm. high, were placed in three vessels, containing each 500 c.c. of (a) common water, (b) 0·1 per cent. of neutral ammonium sulphate, (c) 0·1 per cent. solution of sodium amidosulphonate. In (a) and (b) new rootlets gradually developed, but not in (c). After five days, withering of the leaves commenced in (c), and complete death had happened in nine days, whilst the plants in (a) and (b) were still perfectly healthy.

Young branches of *Prunus Cerasus*, 40 cm. long, were placed in the same solutions and also in 0·1 per cent. of hydrated sodium sulphate. After three days, brown spots had appeared upon all the leaves kept in the amidosulphonate, and, two days later, all these leaves were dried up, whilst in the control solutions the branches still remained healthy, and for a long time afterwards.

Isolated leaves of *Æsculus* and *Morus* behaved in these solutions in the same way. Mr. Maeno made, under my supervision, further experiments with young plants of *Allium fistulosum, Soja hispida,* and *Brassica Rapa*, and in all these cases some noxious action of calcium amidosulphonate became evident. In these experiments, all the mineral nutrients were present.

In contrast to what precedes, algæ (*Spirogyra Mesocarpus*) had not suffered, even in a 1 per cent. solution of calcium amidosulphonate, after a week, whilst the ammonium salt killed them, in 0·5 per cent. solution, within two days.[*]

That mould-fungi and bacteria can utilise amidosulphonic acid as a source of nitrogen was clearly established by their development in solutions containing 1 per cent. of cane sugar, 0·1 per cent. of monopotassium phosphate, 0·1 per cent. of magnesium sulphate, and, as the only source of nitrogen, 0·1 per cent. of amidosulphonic acid, either free or as calcium salt. Mr. Maeno studied the matter closely with beer yeast, and observed that, although the acid can be utilised as a source of nitrogen, it is not so good for the purpose as ammonium sulphate. 10 c.c. of thin beer yeast, corresponding to 0·0613 gram of dry matter, was suspended in a solution containing in 100 c.c. 6·856 grams of glucose, 0·1 gram of magnesium sulphate, 0·2 gram of monopotassium phosphate, and 0·1 gram of sodium amidosulph-

[*] All ammonium salts are, for these kinds of algæ, noxious at this concentration.

onate (A). In a second flask, (B), the last-mentioned salt was replaced by 0·1 gram of ammonium sulphate. After five days the yeast in (A) had increased 169 per cent., and that in (B) 223 per cent., while of the glucose there had been fermented in (A) 48·8 per cent., and in (B) 55·2 per cent.

Finally, it may be mentioned that on lower aquatic animals, as Infusoria, Rotatoria, and Copepoda, calcium amidosulphonate, in a per cent. solution, had no noxious action.

The poisonous action of amidosulphonic acid on phænogams is of considerable interest. Ammonia, in its salts, acts noxiously also, but only in higher concentration; it never is stored up as such in plants as nitrates are, but is quickly converted into an indifferent substance, *asparagine*, as the recent investigations of Kinoshita and Suzuki, in the College of Agriculture, Tōkyō, have placed beyond doubt. It is the failure of the plants to convert amidosulphonic acid into an analogous indifferent substance that, perhaps, gives time for the gradual action of the labile amido-group on the living protoplasm. The poisonous action of the labile amido-groups in hydroxylamine and diamidogen for the most varied organisms is well known. The fact that amidosulphonates are poisonous neither for lower plants like algæ and low fungi, nor for animals (see the ADDENDA to this paper), still needs an explanation that shall be perfectly satisfactory. The corresponding carbamic acid was found by Nencki to have a poisonous effect on animals.

Imperial University,
Japan.

ADDENDA, by EDWARD DIVERS. Further experiments on the physiological action of amidosulphonic acid are in progress in Dr. Loew's laboratory in the Agricultural College of the University, the results of which will appear in the *Bulletin* of the College. When the above paper was written, the fact had not been ascertained that amidosulphonic acid acts as a reducing agent on alkaline silver solutions, apparently becoming oxidised to water, nitrogen, and sulphite. This reducing power brings it into association with hydroxylamine, hydrazine, and amidogen, which Dr. Loew has shown to be so highly poisonous, though only remotely, because its reducing power is so feeble, as compared with theirs. The simultaneous generation of sulphite should add to its poisonous action.

Professor D. Takahashi, of the Medical College of this University, has examined the action of sodium amidosulphonate on vertebrate animals, and has kindly communicated his results to me. He injected 0·2 gram of it subcutaneously into a frog, and intravenously

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1·4 grams into a young dog weighing 2 kilos., in both cases without an injurious effect or any symptoms like those observed by Nencki in experiments with sodium carbamate. Amidosulphonates, therefore, seem not to be poisonous to animals.


CXIII.—*Economical Preparation of Hydroxylamine Sulphate.*

By EDWARD DIVERS, M.D., F.R.S., and TAMEMASA HAGA, D.Sc., F.C.S.

IN 1887, Raschig made known that hydroxylamine can be got from a nitrite by sulphonation followed by hydrolysis, and took out patents for its manufacture in this way. As to what extent these patents may have since been worked, and with what success, we have no information; but we cannot believe that this process has been advantageously carried out, unless the directions he gave have been greatly modified. The one we are about to describe is very productive and economical for the preparation of hydroxylamine sulphate, a non-deliquescent salt readily forming large crystals, and soluble in three-quarters of its weight of water at 20°.

Commercial sodium nitrite of 95 per cent. nitrite does not contain more than 1 per cent. of objectionable matters, such as chloride and nitrate, and is, therefore, pure enough. A concentrated solution of this salt (2 mols.), and of sodium carbonate (1 mol.), pretty closely adjusted in these proportions, is treated with sulphur dioxide until just acid, while it is kept well agitated at 2—3° below zero by immersion in ice and brine; at this temperature, the conversion of the nitrite into oximidosulphonate appears to be perfect. When gently warmed with a few drops of sulphuric acid, the oximidosulphonate rapidly hydrolyses, with marked rise of temperature, into oxyamidosulphonate and sodium hydrogen sulphate. The solution of these salts is kept at 90—95° for two days, by the end of which time all the oxyamidosulphonate will have hydrolysed into hydroxylamine sulphate and sodium hydrogen sulphate; the quantity of ammonium salt produced is so small that it can only be detected in the very last mother liquor of crystallisation, using platinic chloride (potassium hydroxide being an unsuitable reagent in presence of hydroxylamine). At 80—85°, five days are necessary, but then practically no ammonia is formed; at 70°, three weeks, at least, are necessary; whilst at the common temperature much oxyamidosulphonic acid remains unchanged after several months, even when much sulphuric acid has been added. On the other hand, the solution kept boiling needs

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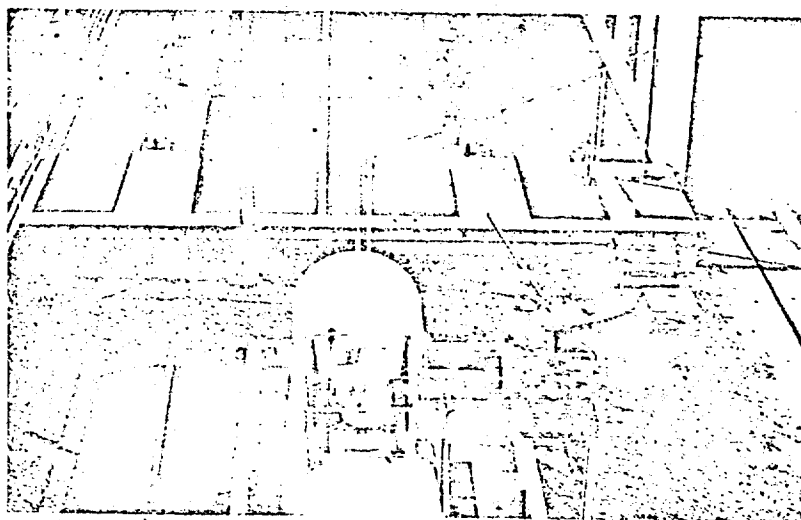
"Low ratios of chlorine [as from chlorine-dosing facility shown] must be considered with great caution."

Commentary–II

J. Carrell Morris

The article by W. Bruce Murray gives an account of an interesting practical application of the known high aqueous stability and residual bactericidal effect of chlorinated sulfamate. It was J. A. McCarthy[1] who originally described the latter, as the result of a study in which successive increments of clarified sewage were added to solutions of chlorinated sulfamate. The great stability was encountered by Dr. Hend Gorchev in her studies of the chemistry of chlorinated sulfamate under the Public Health Service Research Grant RG

4378.[2] She found that prepared chlorinated sulfamate solutions in the laboratory would lose only 1–2 per cent of available chlorine per day, regardless of the chlorine-nitrogen ratio.

It must be realized, however, that chlorinated sulfamate is not a very powerful disinfectant, so that any water supply must be fully disinfected with free available chlorine before sulfamate is added. The studies of Stuart and Ortenzio[3] and, later, the more extensive ones by J. E. Delaney[4] showed that, even with dichlorsulfamate, about 5 ppm (mg/liter) of chlorine was needed for about 30 min to give 99 per cent kill of enteric bacteria. Only for a situation like that in a transmission or distribution main, where the bacteria on the walls are continually in contact with flowing chlorinated sulfamate for days or weeks, can it be regarded as a satisfactory bactericide. There is one biological advantage to chlorinated sulfamate. Unlike free chlorine or chloramine, it seems to be more effective the greater the pH value.

The chemistry of chlorination of sulfamate is not exactly as Mr. Murray has described it. According to Dr. Gorchev's findings, the rate of formation of dichlorsulfamate is so much faster than that of monochlorsulfamate at usual water pH values that better than 90 per cent dichlorsulfamate is always obtained initially, even with sulfamate-to-chlorine ratios as great as 10 : 1.[2] The mixture will gradually revert to the less active monochlorsulfamate over a period of

days, but this reaction is of little significance in water treatment.

The observation that dichlorsulfamate is considerably more active chemically than monochlorsulfamate is a valid one. Delaney[4] found that when ammonia was added to solutions of $NCl_2SO_3^-$ the reaction

$$NCl_2SO_3^- + NH_3 = NHClSO_3^- + NH_2Cl$$
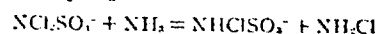
occurred fairly rapidly, indicating the chemical activity is great enough to convert ammonia to chloramine. Incidently, the germicidal nature of the solution increased as this reaction occurred showing that the NH_2Cl is the more active bactericide. On the other hand, monochlorsulfamate could be left in contact with ammonia for days without indication of any transfer of chlorine to ammonia. The monochlorsulfamate in neutral solutions presumably has a lower redox potential than chloramine.

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4. Delaney, J. E. & Morris, J. C. Bactericidal Properties of Chlorsulfamates. Proc. Nat'l Specialty Conf. on Disinfection, ASCE, New York (1971). pp. 61–83.

A CORROSION INHIBITOR PROCESS FOR DOMESTIC WATER

W. Bruce Murray

A technique of corrosion inhibition using a special mixture of zinc sulfate, sulfamic acid, and monosodium phosphate, which will minimize pitting and tuberculation, is described.

CORROSION of metallic plumbing in domestic (potable) water supplies is difficult to control because only certain non-toxic substances at low dosage levels can be employed.
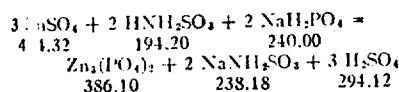
Inhibitor Application

The inhibitor is designed for use by water treatment plants to control the corrosion of both municipal and domestic water plumbing systems. When it is applied to a corrosive water it passivates the surface of a metal because it lays down a controlled film of insoluble zinc phosphate.

The process will protect the common metals against various types of corrosive waters ranging from aerated soft meteorological to high total dissolved solid water supplies.

Inhibitor Formulation

A mixture of materials which has proven successful as a corrosion inhibitor consists of 3 mole parts zinc sulfate, 2 mole parts sulfamic acid and 2 mole parts monosodium orthophosphate:

$$3 ZnSO_4 + 2 HNH_2SO_3 + 2 NaH_2PO_4 =$$
$$\text{3} \quad 4 \quad 1.32 \qquad 194.20 \qquad 240.00$$
$$Zn_3(PO_4)_2 + 2 NaNH_2SO_3 + 3 H_2SO_4$$
$$386.10 \qquad 238.18 \qquad 294.12$$

A aqueous solution containing 1 µ of zinc per gal can be prepared by adding a 50 µ composite of the ingredients to 8.25 gal of water:

```
ZnSO4 · H2O..............27.65 lb
HNH2SO3 .............10.00
NaH2PO4 .............12.35
                        _____
                        50.00
```

The inhibitor solution has the following physical characteristics:

```
Color............water white
Baume..........45.2 @ 20 C
pH..............1.0 @ 20 C
```

Ten gal of the above 5 lb/gal solution applied to 1 mil gal of water will furnish a zinc level of 1.2 ppm.

Inhibitor Dosage

Dosage of the inhibitor to a corrosive water should be applied initially to within 2 to 3 ppm zinc. This dosage should be maintained for a length of time as dictated by the level of zinc sampled at some remote point in the distribution system. When it has been determined that the zinc residual has approached the applied dosage, the zinc treatment rate to the water should be reduced to a continuous dosage of 1 ppm. The estimated length of time required for the initial dosage to passivate a distribution system (including "customer" plumbing) is 3 wk.

In some highly alkaline waters it may be necessary to add 0.5–1.0 ppm of sodium hexametaphosphate so as to prevent the precipitation of calcium carbonate (threshold effect). Calcium carbonate scale must not be permitted to form because it weakens the film protecting properties of the zinc phosphate, and seriously impairs its efficiency as an inhibitor.

Safety

Use of the inhibitor solution at dosage levels of 2 ppm Zn or less has been approved for a public water supply by the Health Department of the State of California.

After 2 yr of application to the distribution system of the City of Long Beach (California) Water Department at a zinc dosage level of 1 ppm, the health department of that city has reported no unusual incidence of gastrointestinal disease or any other water related diseases.

Theory of Passivation

To explain the theory of passivation, consider that the inhibitor at a dosage of 3 ppm zinc or less is being applied to a slightly acid to slightly alkaline water (pH 6.5–8.3). Of the ions contained in the inhibitor (zinc, sodium, hydrogen, phosphate, sulfate and sulfamate)the zinc and phosphate ions instantly precipitate in the water environment as colloidal zinc phosphate:

$$3 Zn^{+2} + 2 PO_4^{-3} = Zn_3(PO_4)_2 \qquad 1$$
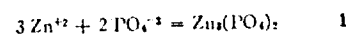
This compound is so finely divided that it resists settling from the bulk of the electrolyte and it can only be removed by centrifuging and ultrafiltration. The zinc phosphate particle is non-polar, non-ionic, rhombic and it has a specific gravity of 3.998. In the freshly precipitated state, zinc phosphate has a very important characteristic in that it adheres as a thin film to most of the common plumbing materials, i.e., metals, glass, plastic or rubber. This film attaches itself so firmly to these substances that it cannot be washed or rubbed off. It is of course subject to mechanical abrasion, and in the presence of a mineral acid or a strong fruit acid it readily dissolves. Metallic pipelines in plumbing systems are subject to zinc phosphate film deposition because the particles are progressively removed from the flowing water stream by collision with the pipe wall. Metals are protected from corrosion since zinc phosphate is insoluble in water at all concentrations and as such it restricts the corrosive effects of the gases, dissolved oxygen and carbon dioxide. Previously rusted or corroded metals are also protected against further attack through film formation on the surfaces of tubercules or other deposits which prevents ion and gas diffusion to the base metal.

Observation of metallic specimens which have been exposed to the inhibitor treated water for a week or longer indicates only a slight loss of sheen. Metal grain, scratches and code stamps can clearly be identified underwater yet when the specimen is per-

FOR PURPOSES OF STUDY

W. BRUCE MURRAY

mitted to air dry, the fine white film of zinc phosphate can be observed. Repeated exposure of the specimen to the inhibitor treated water has shown no increase in specimen weight which would seem to indicate that once a film is formed it is stable and will not continuously deposit on itself.

The most significant factor about the inhibition process is that in controlling corrosion through the deposition of zinc phosphate the water supply is no longer dependent upon the factors effecting calcium carbonate equilibria. For example, a recent test conducted on Aug. 1, 1970 has demonstrated that zinc phosphate will deposit from a high total dissolved solids water (Colorado River water) at any pH from 5.0 to 8.4 and still afford protection to mild steel throughout the entire pH range.

The sulfamate in the inhibitor tightly binds free chlorine so that it theoretically cannot be a factor in corrosion. Chlorine, used by most municipalities as a disinfecting agent, is stabilized by the sulfamate ion according to the quantity of chlorine present:

monochlorosulfamate ion

$$OCl^- + NH_2SO_3^- = NHClSO_3^- + OH^- \qquad 2$$

dichlorosulfamate ion

$$2 OCl^- + NH_2SO_3^- = NCl_2SO_3^- + 2 OH^- \qquad 3$$
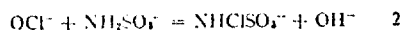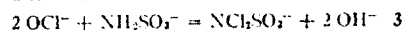
A number of tests, conducted by the Long Beach Water Dept. laboratory, indicate that with a 24 hr contact time, a total bacteria kill was observed with zinc sulfamate at 0.5 ppm chlorine, whereas without the inhibitor twice the chlorine concentration was required to achieve the same effect (see Table 1). Since the phosphate contained in the inhibitor might be a nutrient for bacteria, a dichlorosulfamate residual (one to two mole ppm of chlorine per mole ppm of sulfamate ion) should be maintained in the distribution system. An advantage of maintaining a dichlorosulfamate residual is that it permits a much higher chlorine content without consumer complaint of chlorinous taste. With the adoption of the inhibitor program in 1967, there has been a cessation of taste and odor complaints derived from stagnant water conditions in the dead-end sections of the distribution system as a result of the dichlorosulfamate chlorine residual.

Specimen Analysis

The effectiveness of the corrosion inhibition process can best be detected by specimen observation. At frequent points in the distribution system, particularly in the outer fringe areas, galvanized iron and black iron nipples should be placed in both hot and cold water lines between compression couplings. Compression couplings are used so that the nipples can be easily removed and reinstalled without damage by plumbing tools. For a ¾-in. service a nipple length of 3½ in. is convenient because it permits the nipple to be weighed with a sensitive balance to an accuracy of four places.

Nipple observations in which the interior deposits are not removed but simply air dried prior to weighing, should be conducted monthly. An accumulative weight history of each nipple, along with a brief description of the film or deposits found, is important because it determines whether a system is passivated, whether there are tubercules, and if a film formation is of uniform thickness.

Assuming a ¾ in. × 3½ in. nipple, the corrosion rate or metal loss (or gain) in milligrams per square diameter per day (mD²d) can be computed as follows:

$$mD^2d = \frac{\text{Grams loss (or gain)} \times 1,000}{0.5761^* \times \text{days exposed}}$$

$$= \frac{\text{Grams loss (or gain)} \times 1,735}{\text{days exposed}}$$

Distribution System Experience

The City of Long Beach in 1962 was troubled with a pitting type of corrosion in a blended water portion of the distribution system, and a plugging

* Nipple area (inside) in square decimeters.

type of corrosion in the remainder of the system. Colorado River water was used in a 50 per cent blend with local treated well water in the section of the city experiencing the pitting while straight Colorado River water was responsible for the plugging condition. The reason for the sudden increase in corrosion in 1962 was because the city was suddenly limited to the amount of well water it could produce at that time, and the required volume of water had to be made up with additional Colorado River water, increasing its content from 5 to 50 per cent. Scale and tubercules were present in the mains along with red water (rust) in the dead-end portions of the distribution system. As many as ten complaints of pitting were received per day and a full time flushing crew was required to combat rust, taste and odor complaints. The problem was further intensified in the blended water system by the high chlorine demand of the water which failed to support a post-chlorine dosage of 3 ppm. Caustic soda, lime, sodium silicate, soda ash, phosphates, and other forms of conventional treatment were applied to the waters as a solution to the problem from 1962-67, but these were found to be ineffective and actually intensified the corrosive attack.

Testing Program

A series of 208 tests were conducted with Colorado River water and its well water blends during an inhibitor development period beginning in 1962. Colorado River water was chosen as the target water because of its extreme cor-
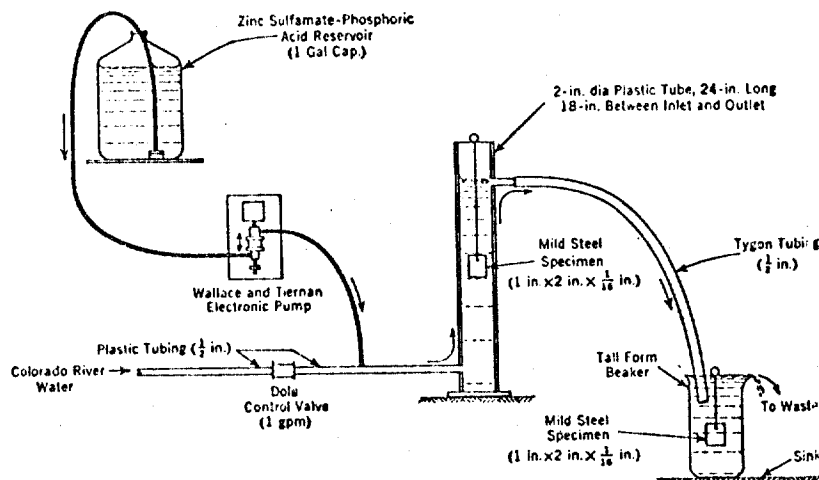

Fig. 1. Corrosion Test Apparatus

TABLE 1
Zinc Sulfamate Disinfection Test
Test performed on a blend of treated well water and Colorado River water.

Cl ppm	Zn* ppm	Number of Colonies							
		1 min	10 min	1 hr	2 hr	6 hr	1 day	2 days	3 days
0	0	22,100	21,600	19,200	19,140	19,200	29,700	21,800	25,000
0.?	0	15,600	14,500	12,500	12,000	800	80	12,100	14,700
0.?	0	12,550	10,400	6,660	6,160	10	21	370	14,200
1.?	0	10,100	9,200	260	49	3	0	0	6,500
2.	0	520	26	300	8	8	210	8,300	28,200
3.	0	70	2	6	2	18	130	11,700	15,800
0	1.0	16,800	14,300	13,200	16,200	16,200	6,400	4,500	7,000
0.0	1.0	4,100	5,400	2,300	380	0	0	0	60
0.5	1.0	3,000	1,900	175	8	4	0	0	28
1.?	1.0	100	29	12	6	2	0	0	9
2.?	1.0	6	17	4	6	0	0	0	8
3.?	1.0	5	4	0	0	0	0	0	65

* As zinc in inhibitor.

Fig. 3. Iron and Galvanized Iron Nipple Weights in a Blend of Hot and Cold Colorado River Water and Local Well Water

ro...vity to metals. This water will cause iron to rust in 15 min and mild steel specimen corrosion rates of 150 mD²d are not uncommon in test specimens removed from the distribution system. Colorado River water is partially zeolite softened to an average hardness of 140 ppm. It has a total solids content of 7?? ppm, chloride and sulfate contents of 125 ppm and 340 ppm, respectively, and a pH of 8.4. The water is oxygen saturated at 10 ppm (18C).

Figure 1 is typical of the apparatus employed for laboratory testing of various inhibitor solutions. A typical inhibitor lasted 30 days in which 43,000 gal of water were processed. Specimens were weighed to four places at the start and conclusion of a particular test and their weights compared to a control specimen in order to determine the efficiency of a certain inhibitor. As an

Fig. 2. Current Versus Time for a Copper Iron Couple in Colorado River Water Dosed With Three PPM Zinc Inhibitor

example, a recent 30-day test using the zinc sulfamate-phosphoric acid inhibitor with Colorado River water at a dosage of 3 ppm zinc + 4 ppm phosphoric acid for seven days, followed with a one ppm zinc dosage and 3 ppm phosphoric acid, yielded the following test data:

Untreated (control)
    specimen—88.17 mD²d
Treated specimen   — 4.55 mD²d

The above represents a 94.8 per cent reduction in corrosion rate.

In a laboratory test conducted Apr. 30, 1969, it was demonstrated that the inhibitor at a 3 ppm zinc dosage passivated iron coupled to copper. In this experiment, two $\frac{1}{4}$-in. diameter bars of copper and iron were placed in parallel $\frac{1}{2}$ in. apart in a flowing stream of Colorado River water, using the apparatus of Fig. 1. A Simpson #269 multitesting meter was electrically connected between the electrodes and the current was measured periodically. Figure 2 summarizes the results of the test in which it can be observed that the current between the couple fell to 50 per cent of its initial value in about 20 hr.

Inhibitor Application

In June 1967, after receiving permission from the State of California to use zinc sulfamate in a public water supply, a dosage of 3 ppm zinc as zinc sulfamate was applied to both the straight Colorado River water and the blended water systems for a period of 2 wk. At this time, the zinc was reduced to a 1 ppm level of both water supplies, a value which has been main-
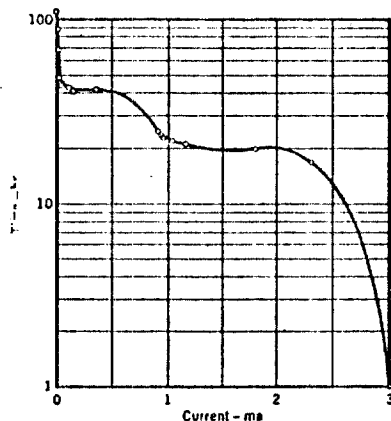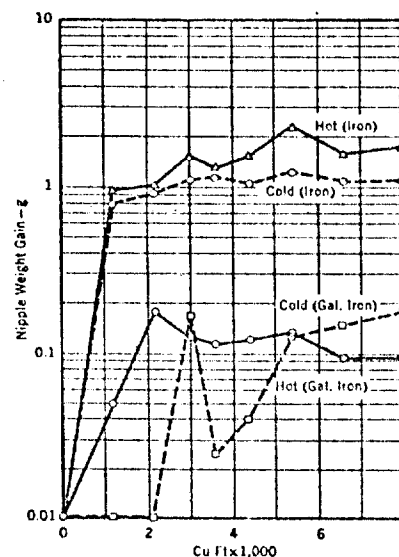
tained continuously up to the present time.

As a result of this program, plumbing pitting and tuberculation complaints have been virtually eliminated. Iron residuals at the extremities of the distribution system have been less than 0.04 ppm. The corrosion rate of mild steel specimens placed at certain fire stations throughout the distribution
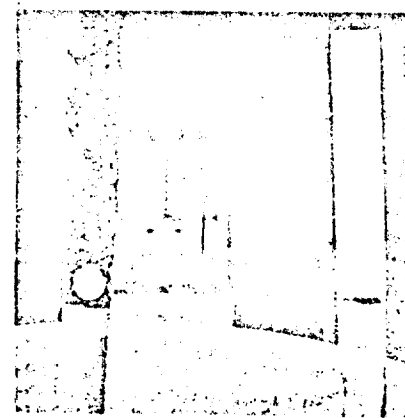

Fig. 4. Effectiveness of Zinc Orthophosphate Inhibitor on Reducing the Corrosivity of Colorado River Water

The carbon steel coupons above were exposed to a 0.5 gpm stream of Colorado River water for 30 days using the tubular test apparatus. The corrosion rate of the control specimen was 85.7 mdd while the inhibitor treated specimen was less than 1.0. Scale analysis indicated that the treated specimen had been zinc phosphatized. The test was concluded on 8-14-70.

system have indicated up to a 95 per cent reduction in corrosion over the previous conventional treatment processes.

Figure 3 demonstrates that the zinc filming tendency of the water is uniform. In a test with the blended water in the distribution system, sets of black iron and galvanized iron nipples were placed before and after a 75 gal capacity hot water tank.* The period represented by the graph is approximately ten months. At the con-

*Temp.--150F.

clusion of each 30 day exposure period, the specimens were air dried, weighed, and reinserted into the system using compression couplings. The curve shows that the thickness of film formation is self-regulating.

Summary

A method of metal corrosion inhibition for domestic water systems has been described which involves the use of a solution composed of zinc sulfamate and phosphate acids.[4]

The inhibitor, applied to a corrosive water at a dosage of 1 to 3 ppm of zinc passivates the surface of a corroding metal by depositing a zinc phosphate film over the surface of the metal, thus preventing the diffusion of DO.

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Taste and Odor Control With Sulfamic Acid

W. Bruce Murray

The author of the initial article reports briefly about the exploitation by his company of a chanced-upon phenomenon. Prior to 1967, some customers were bothered by taste and odor; the addition of sulfamic acid has since resolved the utility's dilemma. The two articles that follow the lead one are commentaries: The first of the two confirms the results of the main article; the second reports that there may be some detracting aspects to an otherwise promising procedure.

The benefits of sulfamic acid were experienced by chance by the Long Beach Water Dept. in 1967 when it was applied to the water supply as a key ingredient for corrosion inhibition.[1] Prior to 1967, a free chlorine residual of 1 ppm would have been nonexistent 1-mi (0.6-km) distant from the outlet of the blended-water distribution reservoir because of the high organic demand. Musty taste and odor would be noticeable in certain sections of the city where a chlorine residual was difficult to maintain.

Then, too, a second typical customer complaint was the noxious odor of hydrogen sulfide gas, which was produced by the oxidation and reduction of bacteria in magnesium anode-equipped hot-water tanks. Flushing programs were practiced in an attempt to draw fresh chlorinated water into problem sections of the distribution system. Increasing the chlorine residuals to values greater than 1 ppm (mg/liter) generally produced customer complaints of chlorinous taste and odor in the immediate vicinity of the reservoir discharge. Although there was no evidence of bacteria of intestinal origin (*E. coli*), most sampling locations throughout the distribution system indicated bacteria concentrations "too numerous to count" (TNTC).

After receiving permission to use sulfamic acid in drinking water from the State of California, its application to the treated water provided an unexpected solution to the taste-and-odor problem. Used in conjunction with chlorine in a community water supply, sulfamic acid has some interesting applications:

1. It is an effective sterilizing agent.
2. It provides stable, long-lasting chlorine residuals.
3. It permits the use of large chlorine residuals—i.e., 2–5 ppm—without public detection.
4. It prevents the oxidation of manganese and the formation of chlorophenols.

By prolonging combined chlorine residual in the distribution system (particularly in low circulation or stagnant areas), taste and odor are sharply reduced indirectly with the destruction of bacteria and certain water-main growths.

The change in the water supply was due to the fact that a 1.5–2.5-ppm (mg/liter) post chlorine dosage, applied with a 1-ppm (mg/liter) dosage of sulfamic acid, was detected as a 0.5–1.2-ppm (mg/liter) combined chlorine residual throughout the entire distribution system. Bacterial counts were reduced to less than 20 as a result, and there was a complete cessation of hydrogen sulfide hot-water-tank-odor complaints.

Chemistry and Dosage

Sulfamic acid is a dry, white inorganic crystalline powder that has a strength approaching sulfuric acid. It is most easily applied by forming a $\frac{1}{2}$-lb/gal ($\frac{1}{2}$-kg/liter) solution and injecting it into the water supply with a metering pump. The material can be used along with post chlorination at dosages ranging from $\frac{1}{2}$ to 3 ppm (mg/liter)—a dosage of 1 ppm (mg/liter) being typical.

Chlorine is stabilized by the sulfamate ion according to the quantity of chlorine present. A dichlorsulfamate ion is produced when 2 mole parts of chlorine are combined with 1 mole part of sulfamate:

$$2OCl^- + NH_2SO_3^-$$
$$= NCl_2SO_3^- + 2OH^- \quad (1)$$
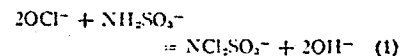
If 1 mole part of chlorine (or less) is entered into solution with 1 mole part of sulfamate, a monochlorsulfamate ion is formed:

$$OCl^- + NH_2SO_3^-$$
$$= NClHSO_3^- + OH^- \quad (2)$$
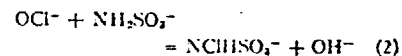
The two combined chlorine end products have entirely different characteristics. The dichlorsulfamate residual possesses an oxidizing capability equivalent to that of free chlorine. This fact was demonstrated by comparing the bleaching rates of the materials on the organic dyes thymol blue and methyl red.

The dichlorsulfamate has the unusual feature of a slow-release oxidizer, which functions at a rate proportional to the amount of organic matter present. Since it is also a less harsh bleaching agent than free chlorine, the dichlorsulfamate formulation is used by industry to prepare cotton, wool, and paper goods.

The monochlorsulfamate residual, on the other hand, displays very little oxidizing capacity and forms slow color-development end points upon the addition of orthotolidine. Although both types of chlorine residual are effective in sterilizing and disinfecting water, the monochlorsulfamate residual with its low oxidation potential should be used in waters containing manganese or phenolic compounds. Iron is unfortunately oxidized by this product but at a considerably slower rate than free chlorine.

Summary

Sulfamic acid at a dosage of 1 ppm (mg/liter) in a domestic water in combination with post chlorine dosages of $\frac{1}{2}$–$2\frac{1}{2}$ ppm (mg/liter) will provide an effective long-lasting chlorine residual that discourages the formation of taste and odor in the domestic water.

Reference

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Possible daily intakes of NAS Appendix A
    substances (Groups I & II), per food category
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Comprehensive GRAS Survey ... NAS/NRC

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Usage levels reported for NAS appendix A
  substances (Group I) used in regular foods
  (table 2)
Comprehensive GRAS Survey ... NAS/NRC

National Academy of Sciences. 1972
Usage levels reported for NAS appendix A
    substances (Group II) used in infant formula
    products and baby foods (B) (table 3)
Comprehensive GRAS Survey ... NAS/NRC 1972

Am. Brew. 86 (10): 43-44, 1953

SULFAMIC ACID for BEERSTONE

REMOVAL and CLEANING PURPOSES

in the BREWING INDUSTRY

By J. Fred Neumeister Sr.

Master Brewer

Diamond State Brewery, Inc.,
Wilmington, Del.

BEERSTONE removal has always been a problem in the brewing industry and most of the strong acids — sulfuric, nitric, and hydrochloric — have been used for this purpose. For some months we have been experimenting with sulfamic acid, an acid that is highly effective in dissolving beerstone and which may be new to the brewing industry.

Sulfamic acid has the chemical formula $HO \cdot SO_2 \cdot NH_2$. It is a crystalline product that is non-volatile, non-hygroscopic and odorless. The acid is soluble in water to the extent of 24.2 gm. per 100 gm. (about 2 lb. per gallon of water) at 25°C. (77°F.). The solubility almost doubles in water at 80°C (176°F.), (47.1 gm. per 100 gm. of water or a little less than 2 lb. per gallon).

Since the acid is a dry product it is readily and safely stored. Dissolved in water, however, it becomes a strong, highly ionized acid as Fig. 1 shows. A 0.5 molal solution of sulfamic acid (4.85%) has a pH of 0.6 while a sulfuric acid of similar strength has a pH of 0.25, both very low pH values, indicating very strong acids compared to lactic acid for ex-

ample, in which a 0.5 molal solution (4.5%) has a pH of 2.1.
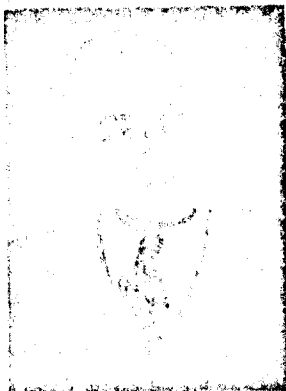
J. Fred Neumeister Sr.

Effect on Metals

Corrosion of metals by sulfamic acid solutions goes on at a slower

rate than with other strong acids. Even copper is less strongly attacked by sulfamic acid than by sulfuric acid so that the danger of injury to metal equipment is reduced when it is used for beerstone removal. On the other hand the sulfamates or salts of sulfamic acid are all highly soluble in water, a property favoring its use for solution of the calcium compounds commonly occuring in beerstone.

When diluted one pound to four gallons of water, sulfamic acts at a surprisingly fast rate on beerstone in Mammuted or glass-lined tanks. The solution is brushed over the tank lining with a tank brush. The usual cleaning operations follow after an hour's contact of the acid with beerstone. Approximately 90% of the beerstone disappears in this first ap-

TABLE I
SOLUBILITY OF INORGANIC SALTS
GRAMS SALT PER 100 GRAMS OF
WATER AT 25°C.

	Sulfamate	Nitrate	Acetate	Chloride	Sulfate
Ammonium	216	214.2	234	39.3	76.7
Sodium	125	91	50	36	28
Magnesium	112	75.4	65.5	56.7	26.8
Calcium	79	138	34.2	90	0.208
Barium	29	10.4	77.3	37	0.00026
Zinc	115	126	44.5	425	57.9
Lead	218	58	55	1.08	0.004

pH. CONCENTRATION CURVES COMPARING
SULFAMIC ACID WITH OTHER ACIDS

Fig. 1

TABLE II
RELATIVE CORROSION RATES OF 3%
AQUEOUS SOLUTIONS OF ACIDS AT
72°+4°F.
SULFAMIC ACID == 1.0

Metal	Sulfuric Acid	Hydrochloric Acid
1010 Steel	2.6	4.2
Cast Iron	3.2	3.2
Galvanized Iron	63	RC
Tin Plate	81	23
304 Stainless	10	VR
Zinc	2.2	RC
Copper	1.5	6.7
Brass	1.5	2.8
Bronze	4.0	7.0
Aluminum	0.6	5.3

RC = Rapid Corrosion
VR = Very Resistant

peratures that are mentioned above should be adequate to cover most situations. Additional experiences with the acid will find it adaptable to many places requiring an acid cleaner.

Because the acid is dry and crystalline, breakage and spillage causes little loss and no damage. The dry crystals do not irritate the skin by simple contact but moisture makes them irritating and they should be removed by flushing the skin areas affected with water. Sulfamic acid has a very low order of toxicity. Normal rinsing should remove all of the acid; however the amounts that might remain in beer through insufficient rinsing of a tank, for example, would be unlikely to affect either the beer or a consumer of it.

The acid is available in 400 lb. barrels and in 50 and 100 lb. fiber drums.

Annual Reports Cited

Fourteen brewing companies were among the industrial corporations and financial institutions which received the merit award of the *Financial World* for producing informative annual reports for 1952. The companies are:

Anheuser-Busch, Inc.
Drewrys, Ltd., U.S.A.
Falstaff Brewing Corp.
Fort Pitt Brewing Co.
Frankenmuth Brewing Co.
Goebel Brewing Co.
G. Heileman Brewing Co.
Lone Star Brewing Co.
Minneapolis Brewing Co.
Pfeiffer Brewing Co.
Jacob Ruppert
Sicks' Breweries, Ltd.
Sicks' Seattle Brewing & Malting Co.
Sterling Brewers, Inc.

One company in the industry will be selected from them by a board of judges to receive a bronze "Oscar of Industry" trophy this month.

plication and a second application removes the remainder of it.

Solution Percentages

Since the first use of this solution containing one pound of sulfamic acid to four gallons of water (3% solution), a 2% solution (26 oz. to ten gallons of water) has kept the beerstone under control. For use on glass-lined tanks a solution of 150-160 deg. F. has quicker action on the deposit. A mixture of sulfamic acid and yeast is also useful (to insure proper coverage of the tank surfaces).

Stainless steel and aluminum kegs can be kept free of beerstone with a dilute sulfamic acid solution. Concentrations of 0.2 to 2% (2.6 to 26 oz. to 10 gallons of water at 150-

160°F.) circulated through the kegs for ten to thirty minutes will usually do the job. After this treatment put the keg through the washing machine.

A paste of yeast, sulfamic acid and waste diatomaceous earth (from beer filtration) makes a good copper cleaner. A solution of 4 oz. of acid per gallon of liquid should be used. The mixture has been applied to kettle and open beer coolers with success and less effort than is required for many cleaners of this type.

Because of the many variations in equipment, composition and heaviness of beerstone deposits, and preferences in cleaning practices, precise recommendations for every cleaning job cannot be given. The range of sulfamic acid concentrations and tem-

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THE PRACTICAL DISINFECTING VALUE OF SOME ACIDS AND ALKALIES AS REVEALED BY THE A.O.A.C. USE-DILUTION TEST

by L. F. ORTENZIO, J. L. FRIEDL, and L. S. STUART
Bacteriological Unit, Pesticide Regulation Section, Plant Pest Control Branch
Washington, D. C.
Delivered by L. S. STUART

Various acids and alkalies are commonly sold as disinfectants. It has been recognized for a long time that the evaluation of such materials by the phenol coefficient procedure does not provide a very reliable index to the necessary concentrations for effective disinfection in actual use. Thus, following the development of the A.O.A.C. Use-Dilution Method[1] all official samples of such materials collected in connection with enforcement activities under the Federal Insecticide, Fungicide, and Rodenticide Act have been checked by this procedure. In general, it can be stated that the results have correlated very well with the practical use recommendations which appear in the literature, although the end points have been at considerably higher concentrations than those obtained in laboratory dilution tube tests. On a few points, the results have been at variance with commonly accepted beliefs. These have been investigated carefully, and it appears that comparisons based on Use-Dilution Method results may bring into focus certain practical limitations with these materials not heretofore clearly understood.

For example, McCulloch[2] reports that "Whitewash made from quicklime and used before the carbon dioxide of the carbonic acid from the air and is converted into carbonate of lime, which is the same as marble and almost totally worthless as a disinfectant."

No consistent differences could be found in the Use-Dilution Method results between various "milk of lime" preparations made from freshly slaked CaO (reagent grade), Ca(OH)$_2$ (reagent grade—carbonate free), freshly slaked commercial samples of quicklime or commercial samples of hydrated lime containing up to 50 percent of carbonates. In every case, the preparations failed to disinfect. Some of the results are shown in Table 1.

The results in this table indicate that "milk of lime" made from freshly slaked commercial quicklime and commercial hydrated lime may, in some instances, have more antibacterial activity than "milk of lime" made from freshly slaked chemically pure CaO or reagent grade—carbonate free Ca(OH)$_2$. Inasmuch as both Tilley and McCulloch are known to have been careful investigators, it must be assumed that both tested at various times "milk of lime" preparations and found them to be effective germicides. Thus, it seems probable that much of the quicklime made in the early part of this

TABLE 1.

Results Obtained in the A.O.A.C. Use-Dilution Method, Using Salmonella choleraesuis with Various "Milk of Lime" Preparations

Material Used*	Sample Alone No. of Rings Tested	Sample Alone No. of Rings Pos.	Sample Alone No. of Rings Neg.	Sample + 1.2% NaOH No. of Rings Tested	Sample + 1.2% NaOH No. of Rings Pos.	Sample + 1.2% NaOH No. of Rings Neg.
CaO (reagent grade)	10	10	0	10	0	10
Ca(OH)$_2$ (reagent grade—CO$_3$ free)	10	10	0	10	0	10
Commercial Quicklime	10	8	2	10	0	10
Commercial Hydrated Lime #1	10	7	3	10	0	10
" " " #2	10	10	0	10	0	10
" " " #3	10	8	2	10	0	10
" " " #4	10	10	0	10	0	10
" " " #5	10	8	2	10	0	10

air has converted the calcium hydroxide into calcium carbonate is effective . . ." Likewise, Tilly[3] states "Ordinary quicklime is one of the best and cheapest disinfectants. It is not commonly applied in the form of quicklime, but in the form of a thick mixture with water known as 'milk of lime.' The lime is first slaked by adding 1 pint of water to 2 pounds of quicklime. . . . milk of lime is obtained by adding 4 volumes of water to 1 of the slaked lime and mixing thoroughly. Lime that has been exposed to the air for a long time becomes air slaked; that is, it takes up moisture and

century carried impurities of a nature that made "milk of lime" preparations effective disinfectants.

A study of the available analytical data on commercial lime samples reveals very little in the way of specific information on the nature of the impurities which might have been responsible. However, it is known[4] that improvements in the methods of burning limestone since 1900 include the replacement of wood with coal in most of the vertical mixed feed kilns, the gradual replacement of the mixed feed vertical kilns with vertical kilns equipped with fire-boxes for burning

coal, oil or natural gas—more recently by center burning gas-fired kilns, and rotary kilns employing mechanically controlled oil or gas burners. The over-all effect of the above changes has been improved chemical and physical control over the specific properties desired in various basic commercial uses and the production of more pure lime. The old mixed-feed vertical kilns produced lime naturally contaminated with ash.

It seems reasonable to assume that the ash contamination where wood was employed as fuel probably resulted in quicklime carrying a relative high percentage of K_2O, and this is the only minor ingredient other than Na_2O to which germicidal activity might logically be attributed.

Studies were conducted, therefore, in which small amounts of NaOH and KOH were added to the lime samples listed in Table 1, and it was found that the addition of 1.2 percent of NaOH or KOH on the basis of the weight of the hydrated lime contained in experimental "milk of lime" preparations was sufficient to bring about a germicidal effect in every instance. The results of some of these tests have also been listed in Table 1. White-washing tests on scraped boards contaminated with chicken feces using the preparations listed in Table 1 and the destruction of gram negative enteric bacteria as an index of effectiveness gave excellent correlation with the results reported therein. It seems evident, therefore, that quicklimes containing appreciable amounts of potash as an impurity could be expected to produce germicidal "milk of lime" preparations. It is obvious, on the other hand, that most quicklime and hydrated lime presently commercially available cannot be relied upon to produce "milk of lime" that will disinfect in the absence of added lye.

Other alkalies which have been designated as germicidal were also tested by this method using both S. choleraesuis and M. pyogenes var. aureus. The results of these studies are summarized in Table 2.

The results in this table are in line with the generally accepted belief that gram negative organisms are more susceptible to the action of strong alkalies than gram positive organisms. It is interesting to note that the concentrations necessary to kill the gram negative organism in this method range from 2.5 to 7 times as high as the concentrations previously reported to be effective against organisms of this type in dilution tube or phenol coefficient-type tests. Also, that this test procedure appears to exaggerate rather than depreciate the differences in effectiveness against gram negative and gram positive organisms.

TABLE 2.

Germicidal Activity of Alkaline Salts

Alkaline Salts	Lowest concentration effective against S. choleraesuis	Lowest concentration effective against M. pyogenes var. aureus
	Percent	Percent
KOH	0.5	5.0
NaOH	0.5	5.0
Na_2CO_3	5.0	>30.0
$Na_3PO_4 \cdot 12H_2O$	7.0	>30.0
$Na_2SiO_3 \cdot 9H_2O$	2.0	5.0

> = greater than

The results with sodium and potassium hydroxides are not inconsistent with the recommendations of Tilley[3] for the use of 2.0 per cent of commercial lye in disinfecting farm premises after outbreaks of virus diseases, fowl cholera and pullorum diseases of young chicks. The results with sodium carbonate and trisodium phosphate clearly emphasize the necessity of adding 0.5 per cent of sodium hydroxide to such other alkaline solutions as 6.0 per cent of washing soda, 2.0

per cent of soda ash, and 2.5 per cent of trisodium phosphate which on occasion have been recommended to disinfect when they are applied at ordinary temperatures as has been pointed out by Tilley.[3]

Some of the acids and acid salts most frequently encountered in commercial acid-type cleaning compounds were also tested by the Use-Dilution procedure. The results are summarized in Table 3.

TABLE 3.

Germicidal Activity of Acids and Acid Salts

Acid or Acid Salt	Lowest concentration effective against S. choleraesuis	Lowest concentration effective against M. pyogenes var. aureus
	Percent	Percent
$NaHSO_4$	2.0	10.0
CH_3COOH	5.0	7.0
$\begin{matrix} CH_2COOH \\ | \\ C\ OH\ (COOH) \\ | \\ CH_2COOH \end{matrix}$	20.0	>30.0
$(COOH)_2$	1.0	2.0
H_2NSO_3H	2.5	5.0
H_2SO_4	4.8	1.9
H_3PO_4	1.7	4.3
HCl	2.6	2.6
H_2SiF_6	0.3	0.3
H_3BO_3	Sat. Soln. ineffective	Sat. Soln. ineffective

> = greater than

In Table 3, it is shown that 2.6 per cent of hydrogen chloride is necessary to give an end point in this method against both gram negative and gram positive organisms, whereas Ostrolenk and Brewer[5] found 0.24 per cent effective against S. typhosa and 0.7 per cent effective against M. pyogenes var. aureus in a dilution tube phenol coefficient type procedure. Thus it would seem that concentrations of from 3.7 to 10.0 times as great are necessary depending upon the organism to kill in the Use-Dilution Method as in the phenol coefficient procedure.

A 2.0 per cent solution of sodium bisulfate was found to be effective against the gram negative organism, and is the concentration commonly recognized as necesary to obtain a germicidal action in cleaning toilet bowls. A much higher concentration of 10.0 per cent was necessary to disinfect against M. pyogenes var. aureus.

Acetic acid was an effective germicide against the gram negative organism at 5.0 per cent and against the gram positive organism at 7.0 per cent. These findings are in general agreement with those reported by Levine and Fellers (1940)[6] and Nunheimer and Fabian (1940)[7] for this particular acid.

Citric acid is a relatively weak germicide; a concentration of 20.0 per cent was necessary to kill the gram negative organisms, and 30.0 per cent was ineffective against the gram positive organism in these studies.

Oxalic acid which is sometimes employed as a minor ingredient in commercial acid disinfectants for urinals and toilets was effective against the gram negative and gram positive organisms at concentrations of 1.0 and 2.0 per cent, respectively. These concentrations, while indicating relatively high activity, are considerably higher than those reported by Reid (1932)[8] as effective against S. typhosa and M. pyogenes var. aureus using dilution tube tests.

Sulfamic acid appears to be twice as active against the gram negative bacteria as it is against the gram positive organism.

The results with sulfuric and phosphoric acids are particularly interesting in that the former is more effective against the gram positive organism than against the gram negative species, whereas the reverse is true with the latter.

Hydrofluosilicic acid was the most active acid as a germicide which was tested, 0.3 per cent being adequate to kill both test organisms in the method. This acid has been proposed for use in disinfecting wooden vats in the fermentation industries.

A saturated solution of boric acid was not an effective germicide.

SUMMARY AND CONCLUSIONS

"Milk of lime" preparations were found to be ineffective as germicides contrary to claims made by accepted authorities. Indirect but substantial evidence has been presented which suggests that the effectiveness of "milk of lime" preparations in disinfecting, observed and reported by investigators in the earlier part of the 20th century, may have been due to impurities in the quicklime employed, probably potash derived from wood employed as a fuel in mixed feed kilns. It seems obvious that 1.2 per cent of sodium hydroxide on the weight of the hydrated lime or 0.3 per cent on a solution basis should be added if "milk of lime" preparations are to be employed successfully as disinfectants.

The concentrations of other alkalines, acid salts and acids required to kill the test organisms in the A.O.A.C. Use-Dilution Method were found to be considerably higher than the concentrations found to be effective by dilution tube testing methods and reported in the literature. On the other hand, they were more in line with the concentrations commonly conceded to be necessary to obtain practical disinfection of inanimate surfaces.

The Use-Dilution procedure appears to provide a more reliable index to the minimum concentrations of acids and alkalies necessary to disinfect inanimate surfaces than dilution-tube methods.

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DISCUSSION

QUESTION: Dr. Stuart, in view of this presentation on the quicklime, will that mean that new labelling on quicklime will have to be taken care of either after a use-dilution test is made, or after a chemical determination is made of the K_2O or the Na_2O content?

Also, I don't recall seeing on the slides a control test in which you took care of plain, ordinary Na_2O or K_2O. Did you have a control test without the quicklime?

DR. STUART: The control tests on sodium hydroxide and potassium hydroxide were shown in the second slide. We didn't list them in the first slide.

I don't think anyone will question the fact that quicklime will act as a disinfectant. The data presented was on "milk of lime" or calcium hydroxide. From a regulatory standpoint, we have numerous manufacturers of land-slaked lime who are occasionally looking around for an advertising gimmick, and they will put disinfecting claims on these packages of lime. Of course, that brings them under the purview of the law which we enforce, and we have to investigate them to see if they are germicidal.

The interesting thing about it is that the theory which is laid down in the textbooks is that calcium hydroxide is inactivated by CO_2 and converted to insoluble carbonate, but we can't find that is true. We can develop no information to bear out this contention. It appeared to us that the activity must be due to some impurity since calcium hydroxide itself is not germicidal.

Actually, most lime manufacturers do not register their products as disinfectants.

QUESTON: They don't, but they sell it to the small fellow who is in the disinfectant business.

DR. STUART: Our experience has been that when you call his attention to the fact that it is not a disinfectant, he is willing to take the claim off the label.

SULFAMIC ACID AND SULFAMATES

Sulfamic acid, NH_2SO_2OH, is the monoamide of sulfuric acid. It was a laboratory curiosity for almost 100 years until new and practical methods of manufacture were discovered in 1936. Rose is credited with the first actual preparation about 1836. The pure acid was prepared later by E. Berglund. Sulfamic acid is produced commercially by reacting urea, sulfur trioxide, and sulfuric acid.

In 1957 the IUPAC Commission on the Nomenclature of Inorganic Chemistry recommended the name "amidosulfuric acid" for sulfamic acid; however, the older name is still in general use.

Principal applications of sulfamic acid are in metal cleaners, scale removers, detergent manufacture, and as a stabilizer for chlorine. The salts of sulfamic acid are used in flame retardants, weed and brush killers, synthetic sweeteners, and for electroplating. Production is some thousands of tons annually for the United States. The selling price for truckloads or carloads in 1968 ranged between \$14.75 and \$16.00 per 100 lb, depending on grade.

Properties

Sulfamic acid is a dry, nonvolatile, nonhygroscopic, odorless, white, crystalline solid. Stability is the outstanding physical property of the acid. In fact, the crystals may be kept in the laboratory for years without change, and are a convenient standard for titrimetry. Other physical properties of the acid are listed in Table 1 (see also refs. 1 and 2).

Table 1. Some Physical Properties of Sulfamic Acid

|	
melting point, °C	205
density, g/cm³	2.126
dissociation constant, 25°C	1.01×10^{-1}
refractive indexes, 25 ± 3°C	
α	1.553
β	1.563
γ	1.568

In aqueous solution it is highly ionized and strongly acidic. The pH of a 1% solution is 1.18. Sulfamic acid is moderately soluble in water; 14.68 g will dissolve in 100 g

of water at 0°C and 47.08 g at 80°C (3). It is soluble in formamide, but insoluble in most other organic liquids.

Sulfamic acid crystallizes in the orthorhombic system with a unit cell of eight molecules. Tablets and compact prisms are obtained from cold aqueous solutions; large, lozenge-shaped plates are obtained on cooling hot aqueous solutions.

Inorganic Reactions. Sulfamic acid begins to decompose at 209°C. At 260°C decomposition produces sulfur dioxide, sulfur trioxide, nitrogen, water, and other products.

Dilute aqueous solutions of sulfamic acid are stable for many months at room temperature. At higher temperatures, however, hydrolysis of the acid and its ammonium salt is comparatively rapid, forming ammonium hydrogen sulfate and ammonium sulfate, respectively.

$$NH_2SO_3H + H_2O \rightarrow NH_4HSO_4$$

$$NH_2SO_3NH_4 + H_2O \rightarrow (NH_4)_2SO_4$$
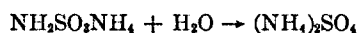
The rate of hydrolysis is regulated by concentration, temperature, and pH (3). Hydrolysis of various concentrations of sulfamic acid at 80°C is illustrated in Table 2.

**Table 2.** Hydrolysis of Sulfamic Acid in Aqueous Solutions at 80°C, %

Time, hr	Solution		
	1%	10%	30%
1	4.54	7.75	7.85
2	9.07	15.07	15.14
5	16.86	28.28	27.49
7	24.18	39.51	37.49

The hydrolysis is highly exothermic, and if a concentrated aqueous solution of ammonium sulfamate is heated in a closed container or one with insufficient venting, it can generate sufficient steam pressure to cause an explosion (4). Amine sulfamates behave similarly. For example, a 60% solution of ammonium sulfamate will begin "runaway" hydrolysis at 200°C at pH 5, and at 130°C at pH 2. However, since the boiling point of a 60% solution of ammonium sulfamate in an open container is 107°C, the hazard of a "runaway" hydrolysis is minimal.

Alkali metal sulfamates are stable in neutral or alkaline solutions, even at the boiling point.

In liquid ammonia, sulfamic acid behaves as a dibasic acid; one hydrogen of the amino group and one hydrogen of the sulfonic group are replaceable by sodium, potassium, etc, to give salts of the formula $NaNHSO_3Na$, etc.

Chlorine, bromine, and chlorates oxidize sulfamic acid to sulfuric acid and to nitrogen.

$$2 NH_2SO_3H + KClO_3 \rightarrow 2 H_2SO_4 + N_2 + KCl + H_2O$$
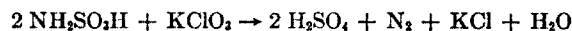
Pure nitrous oxide is obtained by the reaction of concentrated nitric acid with sulfamic acid.

$$NH_2SO_3H + HNO_3 \rightarrow H_2SO_4 + H_2O + N_2O$$
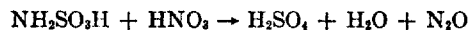
Nitrous acid reacts very rapidly and quantitatively with sulfamic acid, yielding nitrogen gas.

$$NH_2SO_3H + HNO_2 \rightarrow H_2SO_4 + H_2O + N_2$$
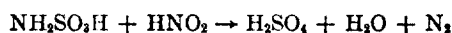
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Hypochlorous acid at low temperature forms N-chlorosulfamic acid.

$$NH_2SO_3H + HOCl \rightarrow NHClSO_3H + H_2O$$
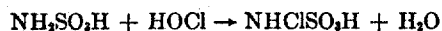
Sulfamyl chloride is formed by reaction of thionyl chloride with sulfamic acid.

$$NH_2SO_3H + SOCl_2 \rightarrow NH_2SO_2Cl + HCl + SO_2$$
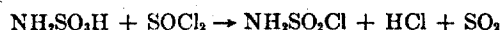
Reaction of certain metal iodides such as those of sodium, potassium, cesium, and rubidium with sulfamic acid forms the triiodides (5).

$$2 NH_2SO_3H + 3 CsI + H_2O \rightarrow CsI_3 + Cs_2SO_4 + (NH_4)_2SO_3$$
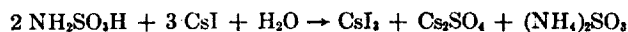
Organic Reactions. Audrieth and co-workers have reviewed the organic reactions of sulfamic acid (6).

Primary alcohols react with sulfamic acid to form ammonium alkyl sulfates:

$$ROH + NH_2SO_3H \rightarrow ROSO_2ONH_4$$

Secondary alcohols react in the presence of an amide catalyst such as acetamide or urea, but tertiary alcohols do not react (7).

Phenol, cresols, xylenols, naphthols, pyrocatechol, resorcinol, hydroquinone, anisole, phenetole, and phenyl ether are sulfonated when treated with sulfamic acid. In most instances, ammonium aryl sulfates are formed as intermediates and the sulfonate results from a subsequent rearrangement. Thus with phenol:

$$C_6H_5OH + NH_2SO_3H \rightarrow C_6H_5OSO_2ONH_4 \rightarrow HOC_6H_4SO_2ONH_4$$

Phenyl derivatives such as anethole, styrene, and isosafrole with unsaturated alkyl side chains are sulfonated in the side chain by reaction with sulfamic acid.

Amides react in certain cases to form ammonium salts of sulfonated amides. For example, treatment with benzamide yields the ammonium salt of N-benzoylsulfamic acid, $C_6H_5CONHSO_2ONH_4$, and, with ammonium sulfamate, yields diammonium imidodisulfonate, $HN(SO_2ONH_4)_2$.

Aldehydes form addition products with sulfamic acid salts. These are stable in neutral or slightly alkaline solutions, but are hydrolyzed in acid and strongly alkaline solutions. With formaldehyde, the salt of the methylol (hydroxymethyl) derivative, $Ca(O_3SNHCH_2OH)_2$, is readily obtained as a crystalline solid.

Cadmium, cobalt, copper, and nickel sulfamates react with lower aliphatic aldehydes. These stable compositions are reported to be suitable for use in electroplating solutions for deposition of the respective metals.

The N-alkyl and N-cyclohexyl derivatives of sulfamic acid are comparatively stable and may be isolated; the N-aryl derivatives are very unstable and can only be obtained in the form of their salts. A series of stable thiazolylsulfamic acids has been prepared.

Sulfation by sulfamic acid has been used, especially in Germany, in the preparation of detergents from dodecyl, oleyl, and other higher alcohols. Secondary alcohols may be sulfated readily by addition of pyridine.

Cellulose sulfated with sulfamic acid has been reported to show less degradation than the customary product from sulfuric acid (8). Cellulose esters of sulfamic acids are formed by the reaction of sulfamyl halides in the presence of tertiary organic bases.

Analysis

Sulfamic acid or the sulfamate ion may be quantitatively determined by reaction with nitrite ion:

$$NaNO_2 + NH_2SO_3H \rightarrow NaHSO_4 + N_2 + H_2O$$
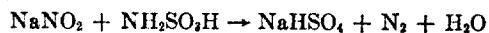
Bowler and Arnold (9) utilized this reaction in a rapid direct titration method using a starch–iodide external indicator. Accuracy was comparable with that of the older gravimetric methods involving oxidation of sulfamate to sulfate. A gasometric method (10) depending on measurement of the nitrogen evolved can be performed with simple apparatus or can be adapted to micro procedures where the accuracy is $\pm 5\%$ and the operation requires only 20 min. The reaction is specific for the amino group and very few ions interfere.

Sulfamic acid and its salts retard the precipitation of barium sulfate. To determine accurately any sulfate derived from hydrolysis of sulfamic acid, it is essential to let the barium sulfate precipitate stand overnight.

Manufacture

Sulfamic acid is manufactured by the reaction of equimolal quantities of urea, sulfur trioxide, and sulfuric acid (11). The reaction, which is strongly exothermic, may be represented stoichiometrically:

$$NH_2CONH_2 + SO_3 + H_2SO_4 \rightarrow 2 NH_2SO_3H + CO_2$$

The reaction is considered theoretically to take place in two steps:

$$NH_2CONH_2 + SO_3 \rightarrow \underset{\text{carbamidomonosulfonic acid}}{HSO_3NHCONH_2} \tag{1}$$

$$HSO_3NHCONH_2 + H_2SO_4 \rightarrow 2 NH_2SO_3H + CO_2 \tag{2}$$

Excess liquid sulfur trioxide may be used as a reaction medium. A liquid mixture of equimolar quantities of urea and sulfuric acid is added to a large excess of liquid sulfur trioxide while agitating and cooling to prevent the formation of carbon dioxide. After completion of the initial reaction, the mass is heated further to produce sulfamic acid. The excess sulfur trioxide is removed by either distillation or spray drying, or both, or by flaking.

The salts of sulfamic acid are manufactured by neutralizing the acid with the appropriate hydroxide or carbonate. Ammonium sulfamate is the most important commercial salt. It is manufactured by adding anhydrous ammonia and sulfamic acid to ammonium sulfamate mother liquor from a preceding crystallization until a hot, concentrated solution of ammonium sulfamate is formed (12). The anhydrous ammonia is added slowly with agitation while the heat of reaction is removed by cooling coils. The hot, concentrated ammonium sulfamate solution is then run to crystallizers from which ammonium sulfamate crystals are recovered; the cold mother liquor is returned to the neutralization step.

Health and Safety Factors

Although brief contact of dry crystalline sulfamic acid with the skin causes no noticeable ill effect, precautions should be taken to avoid contact with the eyes, skin, or clothing. The action of sulfamic acid on the skin is limited to the effects of low pH. It is suggested that both goggles and gloves be worn when handling sulfamic acid dry or in

solution. In the event of contact, flush skin with water; for eyes, flush with plenty of water and get medical attention.

Sulfamic acid presents no fire or explosion hazard and evolves no fumes.

Ammonium sulfamate, like the more common ammonium salts, such as the chloride or sulfate, is neither very irritating to the skin nor very toxic.

Sulfamates

Sulfamic acid readily forms salts by reaction with oxides, hydroxides, carbonates, or active metals. With the exception of the basic mercury salt, its salts are very soluble, particularly the lead salt.

Precise solubility determinations are available for only a few salts (13). The solubility of sodium sulfamate (14) has been determined from 0 to 55°C. At 0°C, 79.90 g dissolves in 100 g of water; at 55°C, 191.30 g dissolves in 100 g of water. Below the transition point (38.3°C), the solid phase in equilibrium with the saturated solution is the monohydrate, a waxy, difficultly filterable material; above the transition point, the anhydrous salt is formed. The anhydrous salt melts at 250°C.

Ammonium sulfamate is five times as soluble in water as ammonium chloride (200.2 g dissolves in 100 g of water at 20°C) and very soluble in glycerol, glycols, and formamide. The pH of a 5% (0.44N) solution is 5.2. Ammonium sulfamate melts at 132.9°C.

King and Hoopes (15) give comprehensive tables of solubilities for calcium, barium, and magnesium salts from 0 to 100°C. The relative viscosity and relative density of aqueous solutions of the acid and the ammonium, magnesium, calcium, and barium salts have been determined for several concentrations at 25°C (16).

Lead sulfamate gives solutions with high densities (2.18 g/ml at 68.5%) which may be used for determining the density of heavy solids.

Uses

Flame Retardants. Ammonium sulfamate is extensively used in formulated, nondurable, flame-retarding agents for cellulosic materials (17). It does not cause stiffening or otherwise adversely affect the hand and appearance of paper and fabrics. Because the sulfamates are water soluble, retreatment is required whenever fabrics are laundered or otherwise subjected to water leaching.

Flame retardants based on sulfamates are used to treat service clothing, drapes and curtains, decorative materials, blankets, and wearing apparel. See Fire-resistant textiles.

Softening Agents. Certain amine sulfamates have been found to have outstanding properties as softeners for paper and textiles (18,19). Compared with other commonly used softening agents, their softening action is longer lasting and is better at low humidities.

Weed and Brush Killers. Sulfamic acid and certain of its salts have proved to be highly effective weed killers. Ammonium sulfamate is a nonselective killer for weeds, brush, stumps, and trees. See Weed killers.

Acid Cleaning. Sulfamic acid is an outstanding choice for acid-cleaning applications. Because of its dry form it is easy to formulate, transport, and handle. It forms soluble salts with most metals and is generally less corrosive to metals than the common inorganic acids (Table 3).

Table 3. Relative Corrosion Rates of 3% Aqueous Solutions of Acids at 72 ± 4°F

Metal	Relative Corrosion Rate (Sulfamic Acid = 1.0)	
	H_2SO_4	HCl
1010 steel	2.6	4.2
cast iron	3.2	3.2
galvanized iron	63.0	a
tin plate	81.0	23.0
304 stainless	10.0	a
zinc	2.2	a
copper	1.5	6.7
brass	1.5	2.8
bronze	4.0	7.0
aluminum	0.6	5.3

a Very rapid corrosion.

These advantages of sulfamic acid have led to its use in acid cleaners in the following fields: in air conditioning for the removal of rust, algae, and hard-water scales from cooling tower systems and evaporative condensers; in marine equipment for the periodic removal of scales from seawater evaporators (distillation units), heat exchangers, and salt water heaters; for cleaning items such as copper-bottomed kettles, steam irons, dishwashers, silverware, toilet bowls, bricks and tiles; in food and dairy processing equipment for removing hard-water scale and protein deposits on cooking and pasteurizing equipment in meat, vegetable, and dairy processing plants. Sulfamic acid is authorized by the United States Department of Agriculture for use in official meat, poultry, rabbit, and egg processing establishments as an acid cleaner for use in all departments.

Sulfamic acid is also used for cleaning steam boilers, condensers, heat exchangers, jacketed equipment, and piping in the chemical process industries (20–22); in brewery equipment for removal of beerstone in glass-lined tanks, kettle and open beer coolers, and beer kegs (23); for cleaning sugar evaporators in both cane sugar and beet sugar refineries (24); in paper mills for conditioning of papermakers' felts, Fourdrinier wires, and cylinder molds, and for descaling black-liquor evaporators and clad digesters (25). Sulfamic acid is approved by the Federal Food and Drug Administration under section 121.101h, "Substances migrating to food from paper and paperboard products used in food packaging that are generally recognized as safe for their intended use, within the meaning of section 409 of the Act" (Food, Drug, and Cosmetic Act as amended, 1958).

Sulfamic acid is used for cleaning or "acidizing" water, oil, and gas wells (26).

Nitrite Removal. One of the first industrial applications to be developed for sulfamic acid is based on its reaction with nitrous acid. This reaction is rapid and quantitative (see above under Analysis). The reaction is applied commercially in eliminatimg the excess nitrite employed in diazotization reactions for dye and colored pigment manufacture, for piece dyeing of fabrics, and for certain types of leather dyeing. In piece-dyeing procedures, sulfamic acid can eliminate all but one of the rinsings normally carried out, with resultant savings in time and water usage.

Other oxides of nitrogen react similarly and can be removed quantitatively and easily from such materials as sulfuric acid and hydrochloric acid.

Electroplating and Electroforming. Most metal sulfamates are soluble and the solutions conduct electricity well; this makes them useful as electroplating salts.

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Deposits from the sulfamates of cadmium, cobalt, copper, indium, lead, nickel, rhodium, or silver, for example, are bright and dense. Plating baths of nickel sulfamate give excellent deposits for electroforming (27).

Baths of aluminum sulfamate are often preferred for the anodic oxidation of aluminum and aluminum alloys. They give abrasion- and corrosion-resistant finishes with good dye receptivity (28).

Sweetening Agents. Salts of cyclohexylsulfamic acid can be prepared directly from sulfamic acid and cyclohexylamine or a substituted cyclohexylamine:

$$2\ RNH_2 + NH_2SO_3H \rightarrow NHRSO_2ONH_3R + NH_3$$
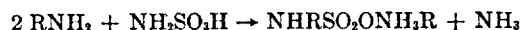
Treatment with sodium or calcium hydroxide gives the corresponding salt, eg $NHRSO_2ONa$ (29). Sodium cyclohexylsulfamate is a well-known sweetening agent. See Sweeteners.

Stabilization of Chlorine. A major use for sulfamic acid is in the broad field of chlorine stabilization. When chlorine gas is dissolved in water, the following equilibrium is established:

$$Cl_2 + H_2O \rightleftarrows HOCl + HCl$$
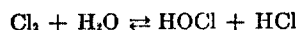
Upon the addition of sulfamic acid, N-chlorosulfamic acid is prepared:

$$HOCl + NH_2SO_3H \rightarrow NHClSO_3H + H_2O$$
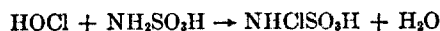
The chlorine here is still active, but the equilibrium with free chlorine is shifted to the right, reducing losses by volatilization; reactivity of the chlorine is also reduced. For these reasons, sulfamic acid is utilized in conjunction with chlorine in such places as swimming pools (30), cooling towers (31), and paper mills (32) to control microorganisms, and in paper pulp for bleaching.

The use of sulfamic acid in paper pulp bleaching is reviewed in a Du Pont Company bulletin (33), and in papers by R. U. Tobar (34), J. M. Robinson and D. Santmyers (35), and L. C. Aldrich (36). Some of the observed benefits include a reduction of pulp degradation, an increase of pulp brightness, and an improvement of bleach plant efficiency.

Analytical Uses. Sulfamic acid has been recommended as a standard of reference in acidimetry (37). The acid is readily purified by recrystallization and air drying to give a stable product analyzing 99.95% pure. A variety of indicators are suitable; bromothymol blue gives a sharp change from yellow at pH 6.4 to blue at pH 7.0.

The procedure for the determination of sulfamic acid with nitrite has been adapted in reverse for the determination of nitrite ion. Sulfamic acid improves the Winkler method for determining dissolved oxygen in water (38). Sulfamic acid is used for removal of nitrites in the Marshall procedure for determining the sulfanilamide content of blood.

Other Uses. Sulfamic acid is used in the sulfation of polyether alcohols. See Sulfonation and sulfation. A number of resins have been prepared by condensing the methylol sulfamates with melamine or urea. Possible uses include water-repellents, sizing materials, and laminating agents. Sulfamic acid has been found to be a good curing agent for phenolics because it has fewer objectionable effects than other inorganic acids and is faster acting than organic acids. Polyamine sulfamates have been shown to produce easier handling crum when used as a coagulating aid for styrene–butadiene rubber (39). Sulfamic acid has been employed as a wash to remove deleterious metallic impurities in the preparation of improved halophosphate phosphors for lamps (40).

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DONALD SANTMYERS AND RALPH AARONS
E. I. du Pont de Nemours & Co., Inc.

Stecher, P.G., Editor. 1968
Ammonium sulfamate; sulfamic acid
The Merck Index - An Encyclopedia of Chemicals
and Drugs, 8th edition

On the Hydrogen Bonds -- Tunnel Effect. Part II. Amidophosphates and

Aminosulphonic Acid

In the infrared spectra of the primary aminophosphates, e.g., $NaPO_3NH_3$,

there occur at 2482 cm⁻ and 2620 cm^{-1} bands of at least medium strength

alongside such bands of the NH valency oscillations at 2900 cm^{-1}.[1]

Analagous bands in the infrared spectrum of aminosulfonic acid have been

hitherto in part neglected[2], in part treated as harmonics[3], in part

referred to the presence of a second type of molecule[4], and in part cited,

but without explanation, as characteristic for the NH^{+3} group beside the

NH-valency oscillations around 3000 cm^{-1}.[5]

The kinship of the absorptions to hydrogen follows from the spectra

of deuterated preparations, aminophosphates exchange hydrogen rapidly.

The infrared spectra of aqueous solutions, in which no trace of these bands

can any longer be observed, show that here it is a question not of harmonics,

but rather of oscillations specifically in the crystal. As is the case in

certain NHN bonds, we assume doubling of the valency oscillation absorptions

of the NHO bonds through the tunnel effect. In addition, an increase in

the number of frequencies occurs as a result of the bond oscillations across

the common nitrogen atom. In the $NaPO_3NH_3$ crystal with the space group

$P6_3-C6_6$[7], the three-fold symmetry of the free ion is preserved, and the

selectivity laws lead one to expect, in the infrared spectrum, a fully

symmetrical and a degenerated bond valency oscillation. In the case of

crystal symmetry[8,9] of aminosulfonic acid, it should have been possible to

observe these degenerations split, and, as a result of coupling of the

eight molecules in the elementary cell, the formation of secondary maxima.

Due to the possibility of harmonics in this range, this cannot be judged with certainty, but (especially in the case of the reduced band width in low temperature absorptions) more absorptions appear than in the case of sodium aminophosphate. In the energy level schema of Fig. 1a, the splittings have been disregarded. In crystal plates of aminosulfonic acid we were able to record harmonics in the 4000 cm^{-1} to 9000 cm^{-1} range. The first are included in the schema of the diagram.

We calculated the potential curve in the NHO bond after the Schroeder and Lippincott model.[10] For DN+--H, we inserted 84.2 kcal/mol; for D_O...H, we inserted 69.0 kcal/mol. R_{NHO} and r_{NH} are known from reference 9. The calculated curve has two minima, cf Fig. 1b. If one assumes G_o 1/2(G_2-G_1) and works with the observed values but without knowledge of the harmonic frequencies, then the level G_1 (mean value of G^{+1} and G^{-1} and of a, and e) lies at the height of the second minimum; the level G_2, lying apparently already above the potential barrier.

Hereby, we believe that type and magnitude of the assumed splittings become readily comprehensible.

(Institute for an organic and an organic-technical chemistry of the Technical University, Dresden.)
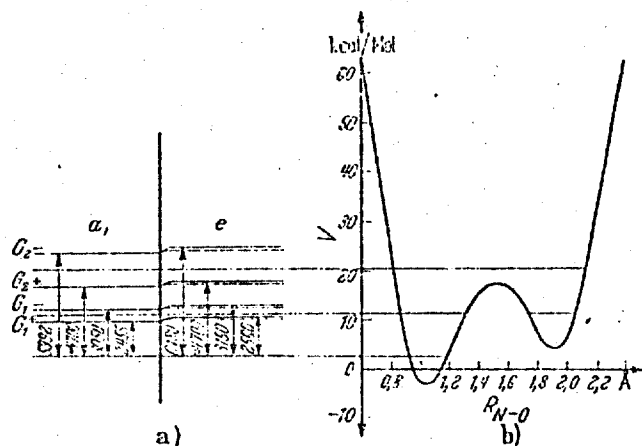
Fig. 1. Comparison of the infrared absorptions observed in amino-
sulfonic acid crystals (a) with a calculated potential curve
(b).

vergleicht, das keine OH-Gruppen enthält und folglich nur noch die Absorptionen der NH ... N (oder O-)Brücken zeigt. Die langwelligere der beiden OH ... O-Absorptionen zeigt zwei Maxima (2150, 2255 cm⁻¹), was man mit der Kopplung zwischen zwei Brücken am gleichen Phosphoratom erklären kann. Für die kurzwellige OH ... O-Bande (≈ 2800 cm⁻¹) entzieht sich dies der Beurteilung durch Überlagerung mit den NH ... N-(O-)Banden (2975, 3075 cm⁻¹).

Beim Oktasilbersalz ist das ganze Gebiet frei von Absorptionen; Oberschwingungen werden bei den verwendeten Substanzkonzentrationen also nicht beobachtet. Bei den Deuteriumverbindungen liegen die Maxima bei 2300 und 2210 cm⁻¹ für NH ... N(O) und bei 1650 und 1720 cm⁻¹ für die langwellige OH ... O-Bande. Die kurzwellige ist ganz verdeckt.

Die Unterschiede in der Größe der Tunneleffekt-Aufspaltung und in dem Ausmaß der Verbreiterung hängen zusammen. (Wir glauben, daß die bisher noch nicht befriedigend erklärte Bandenbreite bei Wasserstoffbrücken-Valenzschwingungen auch vom Tunneleffekt herrührt, und zwar dadurch, daß die für die Größe der Aufspaltung maßgebende Höhe der Barriere zwischen den beiden Minima verändert wird im Verlauf einer Schwingung der schweren Brückenatome[5]). Über die weitere Deutung der Spektren werden wir andernorts berichten.

Wenn der Wasserstoffbrücken-Tunneleffekt nun auch für NH ... N-Brücken vorausgesetzt werden darf, so wird uns die Erklärung der NH-Banden des Phosphams ermöglicht, die mit Maxima von ≈ 3100 cm⁻¹ und ≈ 2700 cm⁻¹ auftreten und von denen die langwelligere mit allem Vorbehalt, aber sicher irrtümlich einer Fermi-Resonanz zugeschrieben worden war[6]). Die Verdopplung der NH ... N-Bande durch den Wasserstoffbrücken-Tunneleffekt ist auch hier wohl die richtige Deutung.

Institut für anorganische und anorganisch-technische Chemie der Technischen Hochschule, Dresden

E. STEGER und K. LUNKWITZ

Eingegangen am 13. März 1961

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Zum Wasserstoffbrücken-Tunneleffekt, II
Amidophosphate und Amidosulfonsäure

In den Infrarotspektren der primären Amidophosphate, z.B. NaPO₃NH₃, treten Banden bei 2482 cm⁻¹ und 2620 cm⁻¹ von mindestens mittlerer Stärke neben den NH-Valenzschwingungen bei 2900 cm⁻¹ auf[1]). Analoge Banden im Infrarotspektrum der Amidosulfonsäure sind bisher teils vernachlässigt[2]), teils als Oberschwingungen behandelt[3]), teils auf das Vorliegen einer zweiten Molekelart zurückgeführt[4]), teils ohne Erklärung neben den NH-Valenzschwingungen um 3000 cm⁻¹ als charakteristisch für die NH₃⁺-Gruppe angegeben worden[5]).

Die Zugehörigkeit der Absorptionen zum Wasserstoff folgt aus den Spektren deuterierter Präparate; Amidophosphate tauschen rasch Wasserstoff aus. Die Infrarotspektren wäßriger Lösungen, wo von diesen Banden nichts mehr wahrzunehmen ist, zeigen, daß es sich nicht um Oberschwingungen, wohl aber um Schwingungen speziell im Kristall handelt. Wie bei gewissen NHN-Brücken[6]) nehmen wir Verdopplung der Valenzschwingungsabsorptionen der NHO-Brücken durch den Tunneleffekt an. Zusätzlich tritt noch Vermehrung der Frequenzen infolge Kopplung der Brückenschwingungen über das gemeinsame Stickstoffatom auf. Im NaPO₃NH₃-Kristall mit der Raumgruppe P6₃—C₆⁶[7]) bleibt die 3-zählige Symmetrie des freien Ions erhalten, und die Auswahlregeln lassen im Infrarotspektrum eine totalsymmetrische und eine entartete Brücken-Valenzschwingung erwarten. Bei der Kristallsymmetrie[8],[9]) der Amidosulfonsäure sollten diese Entartungen aufgespalten und Nebenmaxima infolge Kopplung der acht Molekeln in der Elementarzelle zu beobachten sein. Das ist infolge der Möglichkeit von Oberschwingungen in diesem Bereich nicht sicher zu beurteilen, es erscheinen aber (besonders bei der bei Tieftemperaturaufnahmen verminderten Bandenbreite) mehr Einzelabsorptionen als bei Natrium-amidophosphat. In dem Niveauschema der Fig. 1a sind die

Aufspaltungen vernachlässigt. An Kristallplatten von Amidosulfonsäure konnten wir Oberschwingungen im Bereich von 4000 bis 9000 cm⁻¹ registrieren. Die ersten sind in das Schema der Figur mit eingefügt.

Wir berechneten den Potentialverlauf in der NHO-Brücke nach dem Modell von SCHROEDER und LIPPINCOTT[10]). Für $D_{N^+ - H}$ wurde 84,2 kcal/mol für $D_{O ... H}$ 69,0 kcal/mol eingesetzt; R_{NHO} und r_{NH} sind aus[9]) bekannt. Die berechnete Kurve hat zwei Minima, vgl. Fig. 1b. Wenn man $G_0 \approx \frac{1}{2}(G_2 - G_1)$ annimmt und in Unkenntnis der harmonischen Frequenzen mit den beobachteten Werten arbeitet, so liegt das Niveau G_1 (Mittelwert von G_1^+ und G_1^- und von a_1 und e) in der Höhe des zweiten Minimums, das Niveau G_2 anscheinend schon oberhalb
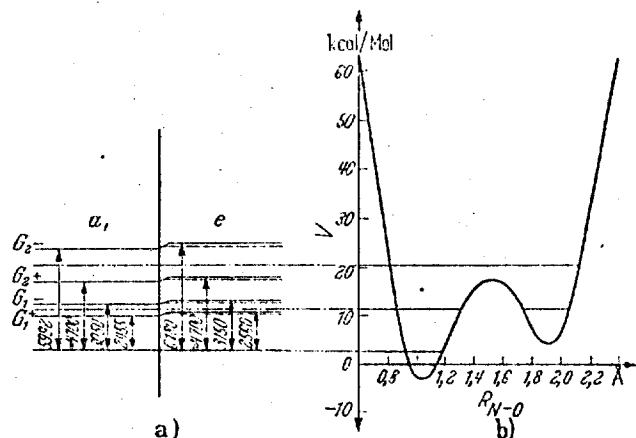

Fig. 1. Vergleich der an Amidosulfonsäurekristallen beobachteten Infrarotabsorptionen (a) mit einer berechneten Potentialkurve (b)

der Potentialschwelle. Damit wird Art und Größe der angenommenen Aufspaltungen unseres Erachtens gut verständlich.

Institut für anorganische und anorganisch-technische Chemie der Technischen Hochschule, Dresden

E. STEGER und K. STOPPERKA

Eingegangen am 13. März 1961

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Die Modifikationen
der Alkali-Bleiphosphate, -arsenate und -vanadate

Bei fast allen Natrium- bzw. Kalium-Erdalkaliphosphaten, -arsenaten und -vanadaten stellten wir Dimorphie fest. Bei Raumtemperatur (RT) sind die rhombisch kristallisierenden Niedertemperaturformen (NT) beständig; bei Temperaturen, die zwischen 680 und etwa 1000° liegen, entstehen hexagonal kristallisierende Hochtemperaturformen (HT), die aber bei RT nicht haltbar sind und wieder in NT übergehen[1]). Wegen der weitgehenden Analogie der Bleiapatite mit den Apatiten der Erdalkalimetalle glaubten wir[2]), daß auch die Natrium-Bleiphosphate, -arsenate und -vanadate die analoge Dimorphie wie die eingangs erwähnten Erdalkaliverbindungen zeigen würden. Allerdings hatten schon MERKER und WONDRATSCHEK[3]) mitgeteilt, daß NaPbPO₄ und NaPbAsO₄ bei RT hexagonal analog den HT der Erdalkaliverbindungen kristallisieren. Wir haben das Verhalten der Bleiverbindungen mit folgenden Ergebnissen nachgeprüft.

a) Bei den *Natrium*verbindungen NaPbPO₄ und NaPbAsO₄ gibt es nur eine Modifikation, nämlich die auch bei RT beständige hexagonale HT[3]). NaPbVO₄ verhält sich ebenso (a 5,59 Å, c 7,01 Å, c/a 1,25). Bei der Synthese dieser Natrium-Bleiverbindungen muß aber Feuchtigkeit ferngehalten werden, und es werden am besten wasserfreie Stoffe umgesetzt, z.B. nach der Gleichung $Pb_2P_2O_7 + Na_2CO_3 = 2NaPbPO_4 + CO_2$.

Thorne, P.C.L., and E.R. Roberts. 1954
Inorganic Chemistry, 6th edition
Interscience Publ, Inc., New York, N.Y.

Sodium thiacyclohexyl sulfamic acid, a new

sweetening agent

by

B. Unterhalt and L. Böschemeyer

From: Department of Pharmacy and Food Chemistry, University
of Marburg/Lahn.

In 1937 Audrieth and Sveda accidentally discovered the sweetening nature of cyclohexyl sulfamic acid and its salts 1, the "cyclamates" (1). In 1950 Abbot Laboratories put its sodium salt on the market under the name of "Sucaryl". We have recently been engaged on the structure-effect relationships of sweetening agents of the cycloalkyl sulfamic acid group and the unsaturated aldoxins (2,3). Our working hypothesis was based on the principle of bioisosterism, for instance the substitution of a CH_2 group in 1 by a hetero atom.

We synthesized the ketones 2 and 3 (4, 5), converted them with hydroxylamine in an alkaline solution into the corresponding oximes 4 and 5 and by reduction with metallic sodium in ethanol we obtained the amines 6 and 7 (6-8). Treatment with freshly distilled chlorosulfonic acid yielded products 8 and 9, either direcly as sodium salts, or after use of a strongly acid cation exchanger, converted via free acids specifically into sodium salts (2).

Please paste in or refer to structural formulas on p. 271.

Ausb. = yield.

While the sodium salt of <u>8</u> did not have a sweet taste,
<u>9</u> in a 0.2% aqueous solution had a degree of sweetness of ca. 8.
Thus while the substance is somewhat less sweet than Na-cyclamate
<u>1</u>, it might be of interest if pharmacologic and toxicologic tests
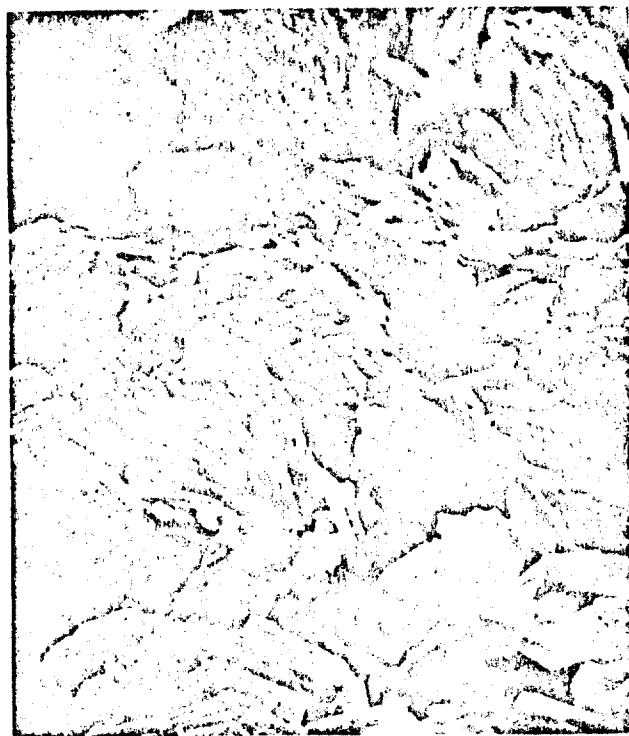are favorable.

Sent in: March 24, 1972.

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Fig. 1. Weißmalschicht einer attischen Lekythos: blättchenförmige, z. T. paketartig gepackte Kaolinitkristalle, die durch Einbrennen der Schicht pseudomorphosiert sind (Rasterelektronenmikroskop, 1 cm = 2 μm)

(zwischen 100—200 μm). Nach dem Habitus zu urteilen, ist ein kaolinitischer Ton verwendet worden, was mit bereits geäußerten Vorstellungen übereinstimmt [7, 8]. Der Kaliumgehalt spricht dafür, daß Pottasche zur Peptisierung des Tones und zur Ansinterung und Verfestigung des Blättchenaggregates zu Hilfe genommen wurde. Die Struktur des Kaolinites ist durch Einbrennen der Malschicht zerstört worden, die Teilchen sind also Pseudomorphosen. Auf einem Scherben erwies sich das Material, abgesehen von einem Quarzanteil, als röntgenamorph, was für die Bildung einer Metakaolinit-Phase spricht. Deren Entstehung ist mit einer Brenntemperatur von ca. 850 °C vereinbar, die für die schwarze Glanztonschicht geschätzt wird [4, 6]. Auf dem anderen Scherben war eine Mullit-ähnliche Phase nachweisbar, die Brenntemperatur hätte danach hier — zum mindesten lokal — höher gelegen. Auffällig ist ein Gehalt an Gips, der in der Größenordnung ≦ 10 % des Tonminerals liegt. Wir halten ihn für sekundär, d.h. durch Staubablagerung oder Berieselung mit gipshaltigen Wässern entstanden; denn auch im Scherben konnte Schwefel nachgewiesen werden.

Eine Überraschung ergab die Untersuchung der Rotmalerei. Während sie auf dem einen Scherben aus α-Fe_2O_3 besteht, ist sie auf dem anderen aus *elementarem Kupfer*. Der unterschiedliche Phasenbestand der Rotmalerei tut sich in verschiedenartiger Tönung der Farben kund. Sie hebt sich im Bruch zwar scharf gegen die weiße Malschicht ab, der sie aufliegt, ist aber offenbar so fein in Kaolinit dispergiert, daß sie als selbständige Phase morphologisch nicht mit Sicherheit nachweisbar ist. Die Gegenwart von Kupfer ist jedoch durch Röntgenmikroanalyse und Debye-Scherrer-Diagramm sichergestellt.

Die griechischen Töpfer bedienten sich also zur Bemalung der Lekythoi verschiedener Techniken. Kupferverbindungen, z. B. Malachit, die hier wahrscheinlich thermisch zu Kupfer reduziert wurden, waren ihnen aus den Minen von Laurion bekannt.

Wir danken den Farbenfabriken Bayer, Leverkusen, für die Unterstützung der Untersuchungen.

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Thiacyclohexylsulfaminsaures Natrium, ein neuer Süßstoff
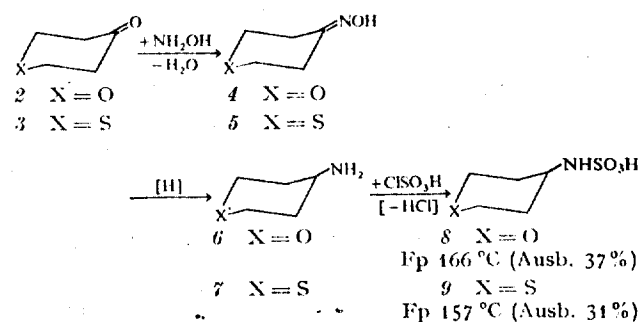
B. Unterhalt und L. Böschemeyer

Fachbereich Pharmazie und Lebensmittelchemie der Universität Marburg/Lahn

1937 entdeckten Audrieth und Sveda zufällig den Süßstoffcharakter der Cyclohexylsulfaminsäure und ihrer Salze 1, der

$$\text{Cyclohexyl}-NHSO_3^{\ominus}$$
1
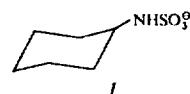
„Cyclamate" [1]. 1950 brachten die Abbott Lab. das Natriumsalz unter der Bezeichnung „Sucaryl" in den Handel.

Seit kurzem beschäftigen wir uns mit Struktur-Wirkungsbeziehungen bei Süßungsmitteln aus der Reihe der Cycloalkylsulfaminsäuren und der ungesättigten Aldoxime [2, 3]. Als Arbeitshypothese dient u.a. das Prinzip der Bioisosterie, z. B. der Ersatz einer CH_2-Gruppe in 1 durch ein Heteroatom. Wir synthetisierten nach bekannten Methoden die Ketone 2 und 3 [4, 5], überführten diese mit Hydroxylamin in alkalischer Lösung in die zugehörigen Oxime 4 und 5 und gewannen durch Reduktion mit metallischem Natrium in Äthanol die Amine 6 und 7 [6—8]. Die Behandlung mit frisch destillierter Chlorsulfonsäure lieferte die Produkte 8 und 9, die entweder direkt als Natriumsalze anfielen oder nach Anwendung eines stark sauren Kationenaustauschers über die freien Säuren gezielt in Natriumsalze umgewandelt wurden [2].

$$\begin{array}{ccc}
\text{2 } X=O & & \text{4 } X=O \\
\text{3 } X=S & & \text{5 } X=S
\end{array}$$

(Reaktionsschema: $2,3 \xrightarrow[-H_2O]{+NH_2OH} 4,5 \xrightarrow{[H]} 6,7 \xrightarrow[{[-HCl]}]{+ClSO_3H} 8,9$)

6   X = O   8   X = O   Fp 166 °C (Ausb. 37 %)

7   X = S   9   X = S   Fp 157 °C (Ausb. 31 %)

Während das Natriumsalz von 8 keinen süßen Geschmack aufweist, findet man bei 9 in 0,2proz. wäßriger Lösung einen Süßungsgrad von etwa 8. Die Substanz ist damit zwar weniger süß als Na-Cyclamat 1, könnte aber bei günstigem Verlauf der pharmakologischen und toxikologischen Prüfung interessant werden.

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TABLE 1

Effect of Chlorine-Sulfamic Acid on Bacterial Count

Elapsed Time hr	Control	1 ppm Sulfamic 0.8 ppm Chlorine		1 ppm Sulfamic 1.6 ppm Chlorine		No Sulfamic 1.6 ppm Chlorine	
	Bact./ml	Bact./ml	Chlorine Residual	Bact./ml	Chlorine Residual	Bact./ml	Chlorine Residual
5	5,500	270	0.20	170	0.80	99	0.75
32	99,000	830	0.07	110	0.60	5	0.30

Commentary-I

Hugo T. Victoreen

A contribution submitted to the JOURNAL on Jan. 10, 1972, by Hugo T. Victoreen (Active Member, AWWA), director of lab., Water Dept., Wilmington, Del.

Free residual prechlorination in a water-treatment plant is of great practical value in improving the quality of water. If it causes the precipitation of certain materials, so much the better they can then be physically removed by flocculation and filtration. If chlorinated organic substances of an odorous character are formed, they can generally be handled by activated carbon fed ahead of the filters. A free residual emerging from a well-run water-treatment plant may show surprising stability, especially in a distribution system consisting of lined mains.

Where chlorination is the *only* treatment practiced, the prospects are less favorable for there is no opportunity actually to remove odorous organics, and particulates in the water will continue to exert a chlorine demand and give protection to microbial life. If one is dealing with a ground water or surface water of low organic and iron content, a free residual may still be the practical choice, but where this is not the case, a combined residual becomes very attractive.

One must be reminded that an oxidizing agent such as free chlorine disappears because it is doing its work. A combined residual, which lasts longer, is by definition oxidizing more slowly. This, of course, is part of the strategy of a water-plant operator using a combined residual. He says, in effect, that he wishes to delay or avoid certain reactions so as to avert odor problems and have chlorine of some sort available in the more remote parts of the distribution system. His final justification for the selection of a combined residual should be to show that it is an effective biocide capable of killing bacteria, actinomycetes, algae, and viruses.

The article from Long Beach, Calif., on the use of chlorine–sulfamic-acid combined residuals is encouraging in two respects. First of all, it reports that these residuals are indeed effective long-lasting biocides.

Second, there is the intriguing prospect of a dichloro form at least as useful to us as the monochloro form. This is a pleasant change from chlorine–ammonia residuals where operators habitually overfeed ammonia in an effort to minimize the proportion of dichloramine formed. Of particular interest is the high oxidizing power of dichlorsulfamate. If it does indeed have the same oxidizing capability as free chlorine coupled with a longer life expectancy, one might be puzzled for a moment over this apparent contradiction in terms, but most would welcome this new tool.

Laboratory Confirmation

In this reviewer's laboratory, experiments have been conducted on a small scale with chlorine–sulfamic residuals. In order to do this the equivalent of a high-quality surface water, which would not require complete treatment, was "put together." It consisted of raw creek water passed through a fiber glass filter and blended with three-day-old tap water that had lost its chlorine. The resulting water had a turbidity of less than 1.0, a 60-min room temperature chlorine demand of 0.8 ppm mg/liter, and a bacterial count of 4,400 per ml as determined by five day 80F (28C) plate counts. Two flasks were dosed with chlorine–sulfamic mixtures, and one was dosed with chlorine only. The fourth flask served as a control. It is apparent from the table that the mixture of 1.6 ppm (mg/liter) chlorine and 1.0 ppm (mg/liter) sulfamic acid was more persistent than the same amount of chlorine by itself. The bacterial population was still declining after 32 hr contact with this mixture. A mixture of 0.8 ppm (mg/liter) chlorine and 1.0 ppm (mg/liter) sulfamic was less impressive despite the fact that 0.8 ppm (mg/liter) was the 60-min chlorine demand of the water. The bacterial population of this flask was climbing at the end of the experiment, and this was the only flask besides the control to show nitrite nitrogen. There was a continuous loss of residual from the flask containing only chlorine, but this was accompanied by an almost complete destruction of the bacterial population.

In the water that was used, the higher ratio of chlorine to sulfamic acid gave good bacterial results although they were inferior to the results obtained with free chlorine. If the water had been more heavily loaded with organic matter, this dichlorsulfamate residual might have shown a clear-cut superiority, particularly if the events had taken place in a water main rather than in laboratory glassware. No odor was detected in any of the flasks, but if such a problem had arisen, it would have strengthened the case for the dichlorsulfamate residual.

Low ratios of chlorine to sulfamic acid must be considered with great caution. The monochlorsulfamate that would be formed in such a situation is a poor oxidizing agent and any excess unchlorinated sulfamic left in solution would probably hydrolyze to ammonium bisulfate, a good bacterial food.

In summary, this reviewer can say that the dichlorsulfamate residual shows considerable promise for those utilities that must produce water with a portion of the chlorine demand unsatisfied. Much more bacterial work is needed on a variety of waters before one can evaluate the effect of dichlorsulfamate on the more-resistant slow growing microorganisms. Where water-treatment plant is available, free residual is still preferable at the prechlorination stage, for free chlorine does not die in vain. It dies in the process of cleaning up the water.

Wodicka, Virgil O. 1971
Regulation of Food and Medicated Animal Feeds
"In Hearings before a Subcommittee of the
   Committee on Government Operations. House of
   Representatives, Ninety-second Congress, First
   Session, March 16-18, 29-30, 1971", U.S. Govt.
   Print. Off., Washington, D.C.

SULFATED NITROGENOUS POLYSACCHARIDES AND THEIR ANTICOAGULANT ACTIVITY[1]

Sir:

N-Deacetylated chitin, previously swollen with pyridine, was heterogeneously sulfated at 100° for 1 hour with chlorosulfonic acid and pyridine to yield a product, isolated (inorganic salts were removed by dialysis) as the amorphous, water-soluble sodium salt, containing essentially two N-sulfate and one O-sulfate groups per anhydrodisaccharide unit; $[\alpha]^{25}D$ −23° (c 1.5, water). *Anal.* Calcd. for $C_{12}H_{16}O_7(NSO_3Na)_2(OSO_3Na)$: C, 22.93; H, 3.05; N, 4.46; S, 15.31; Na, 10.98. Found: C, 22.68; H, 3.08; N, 4.02; S, 15.6; Na, 11.2; −NH₂ (by ninhydrin), absent; NAc, absent. This preparation exhibited the behavior in the Van Slyke amino acid assay characteristic of the acid-labile N-sulfate group present in heparin.[2,3] Its anticoagulant activity was 56 International Units (I. U.)/mg. The animal (mouse intravenous) toxicity was approximately double that of heparin, a finding believed to be due to the unsuitably high molecular size of the substance.

(1) Supported by the Bristol Laboratories, Inc., Syracuse, N. Y., (R. F. Project 432).

(2) M. L. Wolfrom and W. H. McNeely, THIS JOURNAL, 67, 748 (1945).

(3) J. E. Jorpes, H. Buström and V. Mutt, *J. Biol. Chem.*, 183, 607 (1950).

Chondroitinsulfuric acid (from cartilage) was essentially homogeneously N-deacetylated with 45% NaOH (25, 48 hr.) under nitrogen and in the presence of antioxidants (benzyl alcohol and sodium sulfite) and was sulfated as described above (but at 80–90°). The product was isolated as the amorphous sodium salt and is under further analytical characterization; −NH₂ (by ninhydrin), absent. The anticoagulant activity was 48 I. U./mg. The same sample of sodium chondroitin sulfate was subjected to the above sulfation procedure without preliminary N-deacetylation and the product, isolated in the same manner, showed an anticoagulant activity of *ca.* 10 I. U./mg. Sodium heparinate was re-sulfated under these conditions with a reduction in its activity from 110 to 55 I. U./mg. and an increase in the sulfur content from 12 (initial) to 14.4%.

Methyl 2-amino-2-deoxy-β-D-glucopyranoside hydrochloride[4] was sulfated as above to produce the amorphous, water-soluble barium salt of the N-sulfate, tri-O-sulfate; $[\alpha]^{25}D$ +4° (c 3.4, H₂O). *Anal.* Calcd. for $C_7H_{11}NO_{17}S_4Ba_2 \cdot 2H_2O$: S, 15.63; Ba, 33.48. Found: S, 15.64; Ba, 32.98. A 3 × 10⁻⁴ M solution of this substance in 0.004 N HCl at 95° lost 1.0 mole of sulfate in ≤ 20 min. with the concomitant release of the free amino group (ninhydrin). The O-sulfate was removed relatively more slowly and only completely so after 12 hr. Previously reported results[2] on the inactivation of heparin by mild acidity were considered to involve a negligible sulfate loss. On the basis of our present knowledge of the heparin molecule,[5] this sulfate loss is about equivalent to the amino group released so that a sulfate group shift[5] is not a required postulation.

The above results show that the sulfamic acid group is a potent contributor to anticoagulant activity. Experiments are now underway to determine the optimum molecular size for these chemically modified polysaccharides.

DEPARTMENT OF CHEMISTRY   M. L. WOLFROM
THE OHIO STATE UNIVERSITY   (MISS) T. M. SHEN
COLUMBUS 10, OHIO   C. G. SUMMERS

(4) J. C. Irvine, D. McNicoll and A. Hynd, *J. Chem. Soc.*, 99, 250 (1911).

(5) M. L. Wolfrom, R. Montgomery, J. V. Karabinose and P. Rathgeb, THIS JOURNAL, 72, 5796 (1950).

9-21-73

Tracor Jitco, Inc.
1500 E. Gude Drive
Rockville, Md. 20853
Attention: Mr. Donald W. McKinstry

Dear Mr McKinstry

I am sorry to inform you that the use of softening agent with our aerosol inhibitor has been suspended indefinitely as of August 1973. The State of Alabama Public Health Department upon a directive from the FDA stated that it could not be a part of the water supply serving interstate carriers until the phenomenon could be more completely studied.

Yours truly

W. [signature]